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Prediction of the Long Term Stability of Polyester-Based Recording Media

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by

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Abstract

Aging studies with poly(ethylene terephthalate) film base indicate the lifetime is equal to about 1000 years if the material is stored at 20-25°C and 50% relative humidity. Concentration changes of acid and alcohol groups that occur as a result of aging have been measured by infrared analysis. Rate constants calculated by this method agree reasonably well with those calculated from acid contents determined by titration.

Crosslinked polyester polyurethanes were prepared as models of the binder of magnetic tape. Aging studies with these materials indicate that they hydrolyze more slowly than ordinary polyester polyurethanes. Samples aged at 85°C at 100, 50, and 25% relative humidity eventually deteriorated greatly in a physical sense.

Magnetic tapes were aged and measurements made of the sol content of the binder and its adhesion to the polyester base. The latter quantity appears to be a more valuable indicator of tape condition than sol content. Values of binder adhesion of six brands of magnetic tape initially varied between 800 and 35 N/m (or g/cm). Binder adhesion in aged tapes was less the higher the temperature and humidity of aging. A tape transport had difficulty processing tape with values of binder adhesion as low as 10 N/m. There was no problem at 35 N/m. It is anticipated that the lifetime of magnetic tapes can be predicted by measurements of binder adhesion.

1.0 Introduction

A five-year environmental aging study aimed at establishing the lifetimes of magnetic tapes and the poly(ethylene terephthalate) (PET) base of photographic and electrographic film is being sponsored at the National Bureau of Standards by the National Archives. This is the third report on this work.

Data of many kinds are recorded and stored on photographic film and

magnetic tape. Both media contain an active element in a dispersing medium bonded to a substrate of PET. Electrographic film also has a PET base. The lifetime of PET under mild storage conditions is very long but unknown. The iron oxide of magnetic tape is dispersed in polyester polyurethane, a material known to be hydrolytically unstable. Consequently, there is concern about the keeping qualities of film base and oxide binder.

Earlier results in this study agreed with previous work in that hydrolysis appeared to be the most important degradation process. The chemical reaction in both PET and polyurethane is hydrolysis of the ester linkage:

$$H_2O + -CO_2- \xrightarrow{k} -OH + -CO_2H \qquad (1)$$
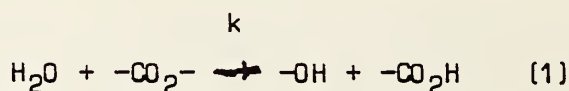
The products of this reaction are an acid and an alcohol; in addition, the polymer chain is broken leading to a reduction in the molecular weight. The previous report showed that the increase in the acid content of PET was approximately equal to the increase in the number of polymer molecules, consistent with reaction 1 being the only scission process. The same result had been found earlier with polyester polyurethanes[1].

Reaction 1 is catalyzed by the acid formed so the hydrolysis rate accelerates exponentially at the small extents of reaction sufficient to seriously reduce the mechanical properties. Applicable equations are:

$$[A] = [A_0] \exp(kt) \qquad (2)$$
$$1/M - 1/M_0 = [A_0](e^{kt} - 1) \qquad (3)$$

Here [A], k, t, and M are acid content, rate constant, time, and molecular weight, respectively. Subscripts indicate use of initial values. The rate constant, k, is pseudo first order because the ester and water concentrations do not change significantly. Physically, k is the fractional rate of increase in the acid content. Values of k are approximately proportional to the relative humidity, RH. Units used for [A] are mol or eq acid/g polymer; these are equal quantities. The quantity $(1/M - 1/M_0)$ represents the mol scissions/g polymer.

The rate constant was calculated from rearranged forms of Eq. 2 and 3, $k=[\ln([A]/[A_0])]/t$ and $k=\{\ln[(M^{-1}-M_0^{-1}+[A_0])/[A_0]]\}/t$, respectively. Values were obtained with PET at temperatures between 115 and 55°C at 100% RH and at 85°C at 100, 50, and 25% RH. The set at 100% RH followed the Arrhenius equation closely. Correlation of acid content with tensile strength and elongation at break indicated that doubling the acid content left tolerable physical properties in the films but tripling it caused serious embrittle-

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ment. Consequantly, Eq. 2 was rearrangad to give t axplicitly and lifetime was assumed to be equal to $(100 \ln 2)/k$ or $69.3/k$ days if k is in %/day. Lifetimes obtained by extrapolation of k to 25 and $20^{\circ}C$ were 400 and 900 years, raspectively, at 100 % RH. Values at 50% RH are twice es long if k is proportional to RH.

The waakest point in tha above enelysis is tha long extrepolation to ambiant tamperature. Most of the axperimentel k are at temperaturas above the gless temperature of PET, about $70^{\circ}C$. The only valua of k at $55^{\circ}C$ was based on a valua of $[A]/[A_0]$ equal to 1.24. This k was on the Arrhanius Line so wa extrapolated linearly below the gless tempereture. Values of k basad on larger $[A]/[A_0]$ and elso et lower temperatures are dasirad to battar validate this extrapolation. Changes in $[A]$ ere very slow et temparaturas of 55 and $35^{\circ}C$. Samples egad at $55^{\circ}C$ are expected to double in acid content in five years; acid contents of those aged at $35^{\circ}C$ may increase by only two percent.

Work on PET in this reporting period has been limited to accumulating data on samples aged at 70, 55, end $35^{\circ}C$ at 25, 50, and 100% RH and developing an infrared analysis based on the increase in concentrations of acid and alcohol groups during hydrolysis.

The polyurethane binder on magnetic tape was expected to obey equations with the same form as those above. Analysis of the reaction is complicated by the large amount of iron oxide suspended in the binder, the presence of lubricants and wetting agents, and the fact that the binder is crosslinked. Additionally, there is evidence that binder becomes more crosslinked at 0 and 15% RH although it degrades at 30 and 100% RH[2]. In the last reporting period we observed this kind of behavior in six kinds of magnetic tape, although our data suggest slow crosslinking even at 30% RH. Cuddihy attributed cross linking to reaction of acid and ester, i.e., the reverse of hydrolysis and predicted that an equilibrium would be reached that would result in more or less permanently stable tape[2]. Later Bertram and Cuddihy settled on $18^{\circ}C$ and 40% RH as the ideal condition for storage[3]. However, soluble polyester polyurethanes do not appear to stabilize at molecular weights sufficiently high to have tolerable physical properties even at 15% RH[4]. Thus there is some uncertainty about what is happening to the binder when magnetic tapes are aged at low RH. Additionally, there is the possibility of the binder becoming detached from the PET backing even if it does not degrade. The binding strength did not deteriorate in tape samples aged at low RH but did at 100% RH[2] and it is uncer-

tain at what RH significant loss in binding strength will occur.

In this reporting period magnetic tapes were aged at several temperatures and RH. Sol fraction and binding force between the magnetic layer and the PET base were measured. Portions of aged tape were tested on a tape transport. Model binder was prepared and aged.

2.0 Experimental

PET samples include coated and uncoated electrographic film, exposed and developed photographic film, and uncoated film base. The National Archives provided all but the uncoated film base, which was purchased. Samples were aged at 70, 55, and 35°C at 25, 50, and 100% RH above solutions of lithium chloride. Tensile strength and elongation at break were measured at intervals on a tensile testing machine. Acid content was measured by titration with tetrabutyl ammonium hydroxide. More details about these methods are given in earlier reports.

Model binders with different crosslink densities were prepared by dissolving a commercial polyester polyurethane in tetrahydrofuran, adding the desired amount of toluene diisocyanate, evaporating the solvent, and curing the film at 100°C under nitrogen for one week. Samples of these films were aged at 25, 50, and 100% RH at 85, 60, and 35°C. Infrared spectra were taken and tensile strength and elongation were measured. Swelling ratio was measured by placing 50 mg. samples in 20 cm^3 of tetrahydrofuran for about 60 hours, decanting the solvent, letting residual droplets evaporate, and weighing the swollen polymer in the closed container. Sorbed solvent was removed under vacuum at 100°C to give dry gel. Densities of solvent and dry polymer were used to calculate the volume swelling ratio by assuming volumes were additive. The sol fraction was calculated by subtracting the gel fraction from one. Some films became completely soluble after aging. Acid contents of these were determined by titration in dimethyl formamide with tetrabutyl ammonium hydroxide.

Six kinds of commercial magnetic tapes were aged at 85, 60, and 35°C at 0, 11, 30, and 100% RH. Aged samples were extracted with tetrahydrofuran to measure the sol content. Binder adhesion was measured by applying sticky tape to the binder layer and using a tensile testing machine to separate the binder layer from the PET base. A tape transport was procured and used to write and read data to and from 50 foot lengths of the aged tapes. The program stopped the test after 25 successful write, read cycles or one unsuccessful one. An unsuccessful attempt was recorded only after several

trials, as determined by the transport characteristics.

Infrared spectra were obtained in a commercial Fourier Transform Infrared, FTIR, machine. Signals from 1000 scans at 8 cm^{-1} resolution or from 100 scans at 2 cm^{-1} resolution were averaged to give the spectra.

3.0 Results

3.1 PET

3.1.1 Aging at 70,55, and 35°C Table I lists tensile strength,T, elongation at break, E, acid content, and k for several kinds of PET after different amounts of aging at 55°C and 100 % RH. There are small but probably significant changes in tensile strength and elongation in most of the samples. Uncoated electrographic film C lost almost all of its ability to elongate.

The acid contents are based on titrations unless use of FTIR is noted. The latter technique is described below but the method is not in its final form so we have not made measurements on all the films. Acid content has increased significantly for all samples tested. Values of k were calculated from the listed acid contents. Uncoated electrographic film C appears to have a higher k than the other films. Unaged, this material had a higher crystalline content than the other films in addition to lower tensile strength and higher elongation.

Tensile strength and elongation did not change significantly when samples were aged at 25 and 50% RH at 55°C or at 35°C at 100% RH for three years. Acid contents have not been measured on these samples.

The long term stability of the various coatings is more questionable than the stability of the PET. Coatings on C and D have changed color even at 35°C. Films aged at 55°C have coatings that are more easily detached than before aging. Some of the changes may be due to light or oxidation, the effects of which will be investigated in the coming period. The photographic films lost the emulsion layer, but only within five cm. of the surface of the LiCl solution used to control the humidity. Positive results were obtained when the denuded areas were tested for Cl^{-}. Apparently there was inadvertent transfer of salt solution to the film. The gelatin of the emulsion layer must have been affected by the salt solution, which has a high ionic strength.

Amorphous PET was aged at 70°C and 100%RH to determine if it accumu-

lated acid at a different rate than semicrystalline commercial films. Unfortunately, it crystallized during aging so we have ended this effort.

3.1.2 Infra red Studies Figures 1 and 2 show FTIR spectra of dry PET between 3800 and 3100 cm^{-1} using 2 and 8 cm^{-1} resolution, respectively. Specimens were three layers of film base each 0.004 in. thick that had been aged in boiling water, as described in the previous report, for the number of days indicated on the plots. Elongation at break and acid content of the film, as measured by titration, are listed in Table II along with differences between the absorbance at 3717 cm^{-1} and absorbances at 3542 and 3256 cm^{-1}.

The FTIR instrument is continually purged with dry air. Sorbed moisture in the films absorbs in the region plotted so spectra changed appreciably for about six hours as the films dried out, but did not change significantly thereafter. There is ample room in the purged space of the instrument for many samples. Opening the purged space briefly to transfer dried samples to and from the sample holder did not noticeably change the spectra. The procedure adopted was to put samples in the purged space the day before they were to be run so that they had more than 16 hours of drying time.

Spectra at both resolutions show increased absorption between about 3600 and 3100 cm^{-1} as the aging time increases. The whole level of absorption seems to increase although a peak at 3542 cm^{-1} becomes more prominent. There are small, regularly spaced peaks in all the spectra that are due to interference between reflections from the front and back of the films. Increasing the resolution sharpens these peaks but does not change the absorption in other ways.

Acid and alcohol groups in PET absorb at 3256 and 3542 cm^{-1}, respectively[5]. Addleman and Zichy have applied infra-red spectroscopy to measure acid and alcohol group concentrations in PET[6]. Their samples had not been artificially aged and acid contents ranged only from 0.49 to 0.59 X 10^{-4} mol/g. Their criterion of dryness was that the sample be more transparent at 3663 than at 3717 cm^{-1}. Our samples dried as described above met this condition. Their method of analysis is considerably more complicated than what we are currently using because they had to allow for differences in crystallinity and orientation, both of which affected the absorption coefficients. Our comparisons are between original and aged material which appear to have the same crystalline content, as measured by differential

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scanning calorimeter. There are no dimensional changes, which would be expected to occur if orientation changed. It is desirable to orient samples consistently in the instrument beam to minimize effects due to dichroism, but these seem to be only a few per cent in our instrument.

Our method is to use the absorbance at 3717 cm^{-1} as the baseline above which to measure absorbance at 3542 and 3256 cm^{-1}. Table II contains absorbance differences that are means of those found in 8 and 2 cm.$^{-1}$ spectra. Fig. 3 correlates the increases in acid content with the increase in absorbance difference. These are reasonably linear correlations. The initial acid content for most films is 0.35 X 10^{-4} mol/g so doubling it should increase the difference in absorbance above that of the base line by 0.2 in the acid region and 0.3 in the alcohol region. There is ample sensitivity to measure that difference so the lines of Fig. 3 could be used to anticipate failure or calculate the rate constant for the increase in acid content. The acid contents with i subscripts in Table I are means of the two values calculated from the lines of Fig. 3.
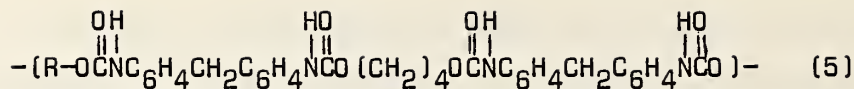
Probably the interfering reflections contribute importantly to the scatter of the data about the lines in Fig. 3. Roughening the samples reduces the reflections but introduces uncertain differences in thickness. One method suggested by Addelman and Zichy[6], which we have not tried as yet, is to coat each film with a dry hydrocarbon.

3.2 Studies with Model Binder[7]

3.2.1 Characteristics of unaged materials The binder layer of magnetic tape consists of iron oxide particles dispersed in a crosslinked polyester polyurethane. This layer is prepared by dissolving a polyester polyure-thane, adding iron oxide and crosslinking agent, applying the slurry to PET film, and heating the film to evaporate solvent and cause crosslinking. The iron oxide is precoated with a wetting agent and a catalyst is used to speed the reaction. A polyisocyanate is used as the crosslinking agent. It reacts with the urethane groups to form allophanate linkages:

$$
\begin{array}{ccc}
\text{OH} & & \text{O OH} \\
\| & & \| \| \\
-\text{OCN}- + -\text{NCO} & --- & -\text{OCNCN}-
\end{array}
\qquad (4)
$$
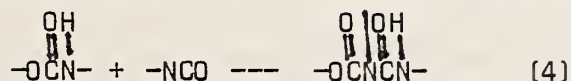
The soluble polyester polyurethane is a block copolymer with the structure:

$$-(R-O\overset{OH}{\overset{||}{C}}N\overset{}{C_6H_4CH_2C_6H_4}N\overset{HO}{\overset{||}{C}}O\,(CH_2)_4O\overset{OH}{\overset{||}{C}}N\overset{}{C_6H_4CH_2C_6H_4}N\overset{HO}{\overset{||}{C}}O\,)- \qquad (5)$$

The group, R, is a polyester, frequently poly(butylene adipate), with a molecular weight of about 1000; it is the soft segment. The rest of structure 5 has a molecular weight of about 600; it is the hard segment and it contains the urethane groups. There are about 15 segments of each type in an average polymer molecule. Hard segments associate to some extent and make the bulk polyurethane behave as if it were crosslinked. The allophanate reaction introduces chemical bonds between hard segments, which may be on different molecules, and so generates an infinite network known as gel. Not every molecule need be part of the gel.

Our model binder lacks iron oxide, wetting agent, and catalyst and it uses a mixture of toluene diisocyanates, 20% ortho and 80% para, instead of a polyisocyanate. Nevertheless, it should respond to hydrolysis much like binder because the hydrolysis occurs in the ester linkages, which are the same in binder and model.

Polymers that have been crosslinked past the gel point are incompletely soluble. They are evaluated by measuring the fraction of material that is soluble (sol,s) and the volume fraction of gel in polymer swollen by solvent. We used these methods and also infra-red spectroscopy to measure the change in acid content. Scission of the ester linkage during degradation creates additional sol, increases the extent of swelling, and increases the acid content, which can not be measured by titration unless the polymer is nearly all sol.

One crosslinked unit per weight average molecule gives gelation[8]. Our starting polymer has number and weight average molecular weights of about 25000 and 50000 respectively, as measured by gel chromatography. Thus only 2×10^{-5} mol crosslinked units/g polymer is required for gelation. Much more crosslinking is possible because each hard segment contains four urethane groups, so there are about 60 possible crosslinking sites per molecule. A network of hard segments is expected if one urethane group in four is crosslinked. This second network should not be degraded by hydrolysis of the ester groups.

Table III lists some of the initial properties of the model binders. Quantities from left to right are: I/U, the ratio of isocyanate to urethane groups mixed together; s, the sol fraction; v, the volume fraction of polymer in a gel swollen with tetrahydrofuran; γ, the number of crosslinked units/polymer molecule; tensile strength; elongation at break; and $\Delta Abs/l$,

the difference in absorbances at 3520 and 3750 cm^{-1} divided by the thickness of the film.

The material with I/U equal to zero is starting polymer. Amounts of diisocyanate much in excess of those theoretically required for gelation were used for the models. Sol fraction decreased and the volume fraction of polymer in swollen gel increased as I/U was increased. Values of γ were calculated from s and v, by equations of Charlesby[9] and Flory[10], respectively. The Charlesby equation was used when I/U was equal to 0.14 and the Flory equation was used with the other two model binders. Sol fractions in these two polymers appeared to be zero, which prevents use of the Charlesby equation. The Flory equation will not allow for crosslinks in the sol, so it was not used when I/U was 0.14. Theoretical values of γ , assuming complete reaction of isocyanate with urethane, are 9,35, and 63 crosslinked units/polymer molecule, at I/U equal to 0.14, 0.55, and 1.10, respectively. The poor agreement with the experimental value at low I/U may be due to crosslinks within one polymer molecule and loss of isocyanate either by evaporation or reaction with inadventitious water. Agreement is better at I/U equal to 0.55 and 1.1 but our aging studies suggest the Flory equation gives too high a crosslink density in this system.

Tensile strength and elongation were measured using rectangular specimens about 2 X 0.3 X 0.01 cm. These had a tendency to tear if the crosslink density was high. The variance is about 25% at I/U equal 0.55 and 1.1 and about 10% at I/U equal 0 and 0.14.

Water contents at 35 and 85°C and 100% RH were nearly the same in the soluble polyester polyurethane and in model binders with I/U equal to 0.14 and 1.1.

Infra-red spectra of aged and unaged dry films between 3800 and 3320 cm^{-1} are in Fig. 4. Lines 1-3 are for unaged film. The large peak that is off the absorbance scale at 3350 cm^{-1} is due to NH stretching. This peak is broader in model binder than in polyester polyurethane. We did not find the acid OH stretching region at 3250 cm^{-1} useful because the NH band was so intense. A useful correlation was developed using the alcohol band at 3520 cm^{-1}. The spectra of unaged films with high crosslink density show smaller absorbance differences between 3520 and 3750 cm^{-1}. The values of ΔAbs/L in Table III quantify this result. It is reasonable because reaction between isocyanate and alcohol is more rapid than the allophanate reaction.

A small sharp peak at 2280 cm^{-1}, a region where isocyanate absorbs, was present in spectra of model binders made with I/U equal to 0.55 and

1.1. This peak disappeared during aging, presumably as a result of reaction between isocyanate and water. Spectra of the polyester polyurethane and the model binder with I/U equal to 0.14 lacked this peak.

A question of importance because of the autocatalytic effect of acid, is whether the isocyanate reacts with carboxylic acid? This is present in the starting polyurethane at a concentration of about 10^{-5} mol/g. Schollenberger and Stewart[11] found no reaction between acid and isocyanate during urethane preparation. Here reaction would compete with the allophanate reaction, which is slow. We aged the polyurethane until it had an acid content of 6 X 10^{-4} mol/g and then treated it with enough monoisocyanate (used so the product would be soluble) to react with all the urethane, alcohol, and acid present. After reaction for one week at $100^{o}C$ the acid content was only 0.25 X 10^{-4} mol/g. Apparently acid can be destroyed by isocyanate.

3.2.2 Aging effects at $85^{o}C$ in model binders

Pieces of the film made with I/U equal to 1.1 were aged in sealed glass tubes above well dried Molecular Sieves in vacuum, dry nitrogen, and dry air. Samples were also aged in wet air at 100% RH and above water vapor in the absence of air. Three exposure times were used: 18.7, 38.7, and 56.7 days. None of the samples that were aged dry swelled less in solvent than it did before aging. Pieces of film made with I/U equal to 0.14 were aged for 10.4 days in dry air and in wet air at 100% RH. The sol fraction of the film aged dry was the same as before aging. Thus our conclusion is that model binder does not crosslink when aged dry. This is a distinctly different result than obtained with magnetic tapes.

The samples aged wet became quite highly colored during aging whereas those aged dry changed very slightly. Fig. 5 illustrates this effect in the films made with I/U equal to 1.1. The unaged specimens and those aged dry barely show in Fig. 5 because they are nearly colorless. Samples aged in vacuum are like those aged in dry N_2. Samples aged wet were at 100% RH except as noted. Discoloration is worse in wet air than in air-free water vapor. There have been studies of the discoloration of polyurethanes during aging[12,13] but the authors did not investigate the effect of moisture.

Samples aged for long periods at high humidity became hard and brittle. Their acid contents actually were less than those of samples aged for shorter times. Our speculation was that the molecules had degraded so much that polyester evaporated and dissolved in the aqueous phase, thereby

raising the glass temperature of the remaining polymer and decreasing its acid content. Samples were submitted for nitrogen analysis; results are in Table IV. The increases in nitrogen content support the hypothesis. Cross-linking and lower RH appear to reduce the effect.

Fig. 6 shows how tensile strength and elongation change with time in samples aged at 100% RH. The lines connect sequential points for each value of I/U. Values for the crosslinked samples usually increase initially. It seems reasonable that scissions in a tightly crosslinked polymer initially increase extensibility. The effect on tensile strength probably is due to decreased sensitivity to edge imperfections in a more extensible polymer. Additional aging causes a rapid decrease in both T and E at times that increase with I/U.

Fig. 7 shows values of T and E after aging at 25% RH. Longer times were required to give the same effects than at 100% RH. The elongations of the two more densely crosslinked samples remain large. Less extensive degradation at 25% than at 100% RH probably gave products that remained in the polymers and softened them. Polymers aged for the longest times are probably too soft to be satisfactory binder even at high I/U.

Agings were also done at 50% RH with results intermediate between those at 25 and 100% RH. All samples eventually broke at low elongation.

Fig. 8 shows the sol fraction of the two more densely crosslinked samples after aging at 25, 50, and 100% RH. The material with I/U equal to 0.55 eventually becomes completely soluble at all RH whereas the other material appears to reach a final sol fraction equal to 0.6. The weight fraction of hard segment plus added toluene diisocyanate is 0.42 when I/U is 1.1. Accordingly, we feel that the material that does not dissolve is primarily crosslinked hard segment, although some hard segment and some ester are in sol and gel respectively. The fact that the polymer with I/U equal to 0.55 did not form permanent gel, even though it had twice the isocyanate sufficient to do so, suggests that at least half the isocyanate was wasted. Crosslinks between urethane groups within the same hard segment or molecule could account for this. An additional implication is that the values of γ in Table III for materials with I/U equal to 0.55 and 1.1 are much too high. The reasons for the failure of the Flory equation may be connected with the preferred association of hard segments in polyester polyurethanes. We suspect that chains coming from hard segment blocks interfere with one another and so do not swell to normal equilibrium.

Values of the sol fraction can be used to calculate the number of

scissions. We did this using the γ of Table III [7] but now think the results were wrong because the initial crosslink densities were too high. Mol scissions/g reached values as high as 4×10^{-3} even at 25% RH. This is much higher than found in polyester polyurethanes at the same RH[4]. More reasonable values are obtained if γ is about 10 for unaged model binder with I/U equal to 0.55. To get this would require that the sol fraction be 0.01, which is too small to be significant. The corresponding density of crosslinked units, γ/M_0, is 4×10^{-4} mol/g if M_0 is 25000 g/mol. The polymer should become completely soluble during hydrolysis when γ is 0.5, since it has a most probable distribution. The concentration of crosslinked units will be unchanged if only the ester groups hydrolyze. Therefore the molecular weight will be $0.5/(4 \times 10^{-4})$ or 1250 when complete solubilization occurs. There should be one acid group per molecule in the degraded material, making [A] equal to 8×10^{-4} mol/g.

Acid content can be measured by titration of soluble polymers. Values obtained by titration of crosslinked, partly soluble polymers are not expected to be valid because the base will not get into the polymer. Infrared spectroscopy appears to be useful in measuring the increase in acid content of such materials.

Lines 4-6 in Fig 4 are infra-red spectra of aged polymers. Comparisons with the spectra of the corresponding unaged polymers indicate the aged samples have a larger absorbance at 3520 cm^{-1}, in the alcohol OH stretching region, and at 3717 cm^{-1}. The absorbance of each sample between 3700 and 6500 cm^{-1} is substantially constant but is higher for the aged films. The cause of this raised absorbance plateau is uncertain but we have treated the flat region as the baseline and measured ΔAbs/l as for the unaged polymers. Titrations for acid were performed on soluble polymers. Acid contents were obtained with unaged starting polymer, I/U=0, and aged polymers with I/U=0, 0.14, and 0.55. As many alcohol groups should form as acid groups, according to reaction 1. Thus one should expect the increase in acid content will be proportional to the increase in the absorbance difference, i.e., $\Delta\Delta$Abs/l. Furthermore, if the original acid content is much less than the acid content after aging, as seems reasonable, then the acid contents should be proportional to the increase in absorbance difference. This is shown to be approximately true in Fig. 9. The line in this figure was used to calculate acid contents of polymers that were not completely soluble.

Fig. 10 is a plot of acid content vs. time at 85°C and 100% RH. Acid

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contents were determined by titration or by use of Fig. 9. Lines are calculated by Eq. 2, using values of $[A_o]$ and k listed on the plots. The intent is to fit only the early points. Figures 11 and 12 contain similar results from samples aged at $85^\circ C$ and 50 and 25% RH, respectively. Note that at 25% RH the last [A] determined for the polymer with I/U equal to 0.55 is about 7×10^{-4} mol/g. The conclusions drawn from these plots are that $[A_o]$ and k are less for the densely crosslinked films.

Presumably reaction between acid and isocyanate reduces $[A_o]$. Reasons for the reduction in k are speculative, but it is suggested that the rate constant for esterification, i.e. the reverse of reaction 1, is effectively greater in a densely crosslinked gel than in an uncrosslinked polymer because the acid and alcohol can not separate normally because of physical constraints. The apparent result would be to decrease k, the rate constant for hydrolysis.

Preliminary tests of this hypothesis have been made by pre-aging model binder and re-aging it at 0% RH. Under this condition the acid content should decrease and hydrolysis should be absent. Reaction is just the reverse of reaction 1. The differential equation connecting [A] and time is[4]:

$$-(d[A]/dt) = k'[A]^2([H_o] + [A]) (6)$$

Here $[H_o]$ is the alcohol content before the initial aging and k' is the rate constant for the back reaction. Acid concentration is squared because acid catalyzes hydrolysis and so must catalyze esterification.

Results in Table V were obtained by integrating Eq 6 and solving the resulting equation for k', using $[A_o]$ as the acid content at the start of the re-aging period and [A] and t as acid content and time after re-aging[4]. Thus each k' is calculated from two points, $[A_o]$,0 and [A],t. The $[H_o]$, which are required, were calculated as follows. The acid content for uncrosslinked polymer was determined by titration and found to be 10^{-5} eq./g. The molecular weight is 20,000–25,000, so there are about 10^{-4} mol of end groups/g polymer. Only 10% of these are acid groups so the concentration of alcohol groups was taken as 10^{-4} mol/g. It was then assumed that ΔAbs/l, in Table III, was proportional to the alcohol content so $[H_o]$ for unaged crosslinked film is 10^{-4} times the ratio of the (Abs/l)'s.

The final column lists the k'. Results probably are not very accurate so the first five listings are regarded as not differing significantly. The last three listings indicate that k' is larger for the most densely cross-linked material. However, the effect seems to be less the greater the

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initial $[A_o]$, i.e. the greater the extent of pre-aging. The implication is that hydrolysis will eventually reduce k' to its value for uncrosslinked polymer. The second listing for k' uses 10^{-4} mol/g for $[H_o]$, which we regard as known only approximately. Larger $[H_o]$ does not eliminate the larger k' of polymer with I/U equal to 1.1.

Previously it was found that k' in uncrosslinked polyester diols and polyurethanes depended on RH[4]. Consequently, the values of k' in Table V probably should not be used at any other RH than zero.

Model binders are being aged at 60 and 35 °C. Preliminary results at 60 °C are like those at 85 °C but a five fold greater time is required to accomplish the same result. No significant degradation had occurred at 35 °C.

3.3 Magnetic tapes

3.3.1 Unaged tapes Characteristics of unaged tapes are listed in Table VI. The values are nearly the same as those in the last report. Changes were made as additional measurements affected the average results. Tape 1 has binder with carbon on the surface opposite the one with magnetic oxide. The other tapes do not have this coating. Several rolls of Tape 5 had very low adhesive force between binder and PET base so the group has been divided into 5A and 5B.

The weight of the binder layer was determined by immersing tape in acetone, scraping off the swollen layer, and weighing the PET base. The organic content of the binder layer was determined by burning off the binder in air. It is possible that some reduction of the iron oxide may have occurred during this operation, which would result in an unknown error. The quantities in the column headed "Sol in Org BL" are probably somewhat more than the sol content of the polymer that makes up the binder layer because of the extraction of additives, such as lubricant, catalyst fragments, and oxide wetting agent.

The acid content of the sol from Tape 4 was measured by titration and found to be 8×10^{-5} mol/g. A lower value was expected because polyester polyurethanes generally are made with acid contents approximately equal to 10^{-5} mol/g. Lower molecular weight components, which have more chain ends and so more acid, tend to remain as sol during crosslinking. This makes the acid content of the sol different from that of the whole polymer but even if there is no acid in the gel the overall value is about 5×10^{-5}. Acid

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contents of sol from other tapes were not measured because they are smaller fractions of the organic component of the binder layer.

The binder layer can be removed from the PET base by immersing tape in the proper solvent mixture for about 60 seconds. A mixture containing three volume percent water in hexafluoroisopropanol works for all except Tape 4. The binder floats off and curls up but has enough strength so it can be drawn flat onto a 10 mil-thick Teflon sheet, that is also immersed. Hexafluoroisopropanol is sorbed by the skin and is a poisonous vapor, so care must be exercised during these operations. Binder on Tape 4 is very fragile when highly swollen, because of its low crosslink density. A mixture of 10 volume percent water in acetone swells the binder layer of Tape 4 adequately. A small amount of material is actually dissolved during the removal operations. The use of mixed solvent and non solvent reduces this to a relatively small fraction of the total sol.

Fig. 13 compares the infra-red spectra of binder layer from Tape 1 and the soluble polyester polyurethane used to make our model binder. The spectra are very similar, except for the scattering due to the oxide particles, which results in a decreasing baseline, and absorption due to the magnetic oxide at about 600 cm^{-1}. There is also a broad, weak peak at 2200 cm^{-1} in the spectrum of the binder layer that is not in that of the polyurethane.

Fig. 14 compares spectra of binder layers from six kinds of tape. All spectra are very similar but there are differences in the weak absorptions between 2600 and 1800 cm^{-1}. The source of these absorptions is unknown. Isocyanates and carbodiimides have relatively sharp absorptions at 2270 and 2170 cm^{-1}, respectively. Isocyanate hydrolyzes to amine at room temperature, so it is unlikely to be present even in unaged tapes. Carbodiimide is used to stabilize polyester polyurethanes and might be an additive, but a narrower peak should result. We had hoped to study the degradation of the binder layer by using the absorption due to alcohol groups, as in model binder, but these absorptions are so weak compared with the scattering that the approach does not appear promising. Signal to noise was much improved by making 10,000 scans, which requires about two hours for each spectrum but even then the desired absorbance difference was not known precisely. Additionally, our aging data suggest that adhesion of binder layer to PET base may be the limiting factor in tape life.

3.3.2 Aged magnetic tapes Tapes 1-5A were aged in vacuum, dry nitrogen, dry

air, wet air (100% RH), and air-free water vapor at 85° C. Aging under dry conditions caused a reduction in the sol content, presumably due to cross-linking. Wet air and water vapor caused approximately equal increases in sol content.

An aging temperature of 85° C appeared more severe than necessary or desirable, since our interest was in changes at ambient temperature. Most of our results now involve agings at 60 and 35° C.

Fig. 15 shows sol contents after aging at 60° C and 100% RH. Most of the tapes reach 5% sol in about 100 days and then give slightly less sol on additional aging. A sol content of 5% corresponds to about 60–70% of the organic component of the binder layer being soluble. Tape 2 reaches only 3% sol, which corresponds to about 55% soluble binder. Even Tape 4 binder, which is 66% soluble to start with, never becomes more than 70% soluble. These results resemble behavior of the most highly crosslinked model binder.

Sol fractions of tapes aged at 60°C and 30, 15, and 0% RH decreased with time, implying that the binder crosslinked. Sol extracted from unaged Tape 4 gelled when aged at 85°C and 0% RH, confirming that crosslinking occurred.

Sol contents of Tapes 1,2,3,4, and 5A are 1.8, 2.4, 4.0, 5.4, and 2.3%, respectively, after about 250 days aging at 35°C and 100% RH. The infra-red spectra of the extracted sol are like the spectrum of the polyester polyurethane in Fig. 13 except for a small sharp peak at 2250 cm^{-1} in the former spectra. Attempts to determine the acid contents of sol extracted from aged tapes by titration have not been successful because color changes during titration preclude use of indicators and no sudden change occurs in electrode potential during potentiometric titration.

Deteriorating adhesive force between binder and PET base could cause failure of the tape. Our method of measuring this force is to apply a 20–30 cm length of 3/8-in wide embossing tape to the center of the oxide layer of the 1/2 in-wide magnetic tape and then separate the two tapes in a tensile testing machine. A high crosshead speed helps start the separation of binder layer and PET; 20 and 40 in/min were used. The force is initially high but decreases quickly and is within about 25% of some average value during most of the pull. There is considerable oscillation of the pen during the pull because the separation occurs as a series of stops and starts. Fig. 16 shows the recorder trace from three such measurements.

Unaged Tapes 2, 4, and 5A do not lose binder layer during these

experiments. The other unaged tapes lose binder, sometimes by failure between binder layer and PET (adhesive) and sometimes by failure within the binder layer (cohesive). Fig. 17 shows the behavior patterns in unaged tapes that do lose binder during the measurement. Most failures are mainly adhesive or mainly cohesive but not exclusively either. Sometimes horizontal or vertical strips of binder layer are left on the PET. There have been cases in which the type of residue has changed within one pull. Fig. 17 contains an example of this. No convincing rationalization of these phenomena has occurred to us.

The measured adhesive or cohesive force decreases during aging in a way that depends on temperature and RH. Binder layer fell off all tapes aged at 60 °C and 100% RH for one year. These tapes were obviously not useful. Fig. 18 and 19 show the time dependence of binder adhesion (or cohesion) after aging at 60 °C and 30 and 15% RH, respectively. Great decreases from the initial values occur. Very low values, about 10 N/m, are reached for Tapes 3 and 6. Aging at 15% RH makes the sol content decrease, so changes in sol content probably will not be reliable indicators of tape reliability.

Values of binder adhesion exceed 80 N/m for all tapes after nearly 500 days at 35 °C and 100% RH. Aging at lower RH for about one year leaves still higher values.

Experiments with aged tapes indicate that write and read problems occur when the binder adhesion value has decreased to about 10 N/m. The programmed write-read sequence, described in the Experimental section, failed after 14 passes of Tape 3, aged until the binder layer adhesive force was 10 N/m. There was binder layer on the heads and when it was removed additional write-read passes were made. Failure again occurred before 25 passes of each type were made. Other aged tapes would run through 25 passes. These results imply that large decreases in binder adhesion can occur before tapes become useless. Consequently, binder adhesion can be used to monitor tape condition.

4.0 <u>Discussion</u>

4.1 <u>PET</u> All results to date indicate that the type of PET now being made will last several centuries under the mild conditions anticipated for storage of archival materials. The extrapolation through the glass temperature is still a source of uncertainty and will remain so until some

determination, probably of the acid content, gives the rate constant at a lower temperature than 55 °C.

It is emphasized that the excellent physical properties of PET may depend on a rather specific combination of orientation and crystallinity. Any changes might result in a material that has different sensitivity to hydrolysis. Results obtained with the electrographic films C may illustrate this. These films fail physically before the other films and have significantly different crystallinity than the other films, as described in the first report.

The infra-red technique described above can be used to monitor degradation, if that becomes desirable. It is necessary to remove any film coating from an area sufficiently large to transmit the beam. The two-fold increase in acid content is a reasonable failure criterion, excepting films C, so long as films of the present type are in use. Changes in film characteristics would require that the failure criterion be reestablished.

4.2 Model Binder The model binders behaved in a manner qualitatively anticipated from results obtained earlier with soluble polyester polyurethanes. There is autocatalysis due to the acid catalyzed hydrolysis. However, times to reach specific acid contents are longer because of the lower initial acid content and, less conclusively, also because of the lower effective rate constants for hydrolysis, Fig. 10 – 12 and Table V. An acid content of 8×10^{-4} mol/g was obtained after long aging of the film with I/U equal to 0.55 at 85 °C and 25% RH. This is about the same as obtained at equilibrium with the soluble polyester polyurethane used to make the model binder[4]. Highly crosslinked model binders became soft and weak at 85 °C even at 25% RH but did not appear to crystallize when cooled to room temperature as did the soluble polyester polyurethanes. Degraded model binder contains allophanate branches which may prevent crystallization. The presence of a network that does not hydrolyze in the most highly crosslinked model did not prevent severe deterioration of the physical properties. Thus the aging results to date indicate that crosslinked polyester polyurethanes do not have sufficiently good physical properties at equilibrium to remain permanently acceptable as binder layer for tape. The main uncertainty in this conclusion is due to the lack of a complete set of data at other temperatures. Such data are being obtained.

4.3 Magnetic tapes Tape binder appears to crosslink at humidities at which

crosslinked polyester polyurethanes degrade. One explanation might be that
initial acid and alcohol concentrations in the binder are sufficiently high
to drive the reaction toward crosslinking. We can make an estimate of what
is required to do this. The relation governing equilibrium is[4]:

$$k[E][W] = k'[A][H] \qquad [7]$$

Here [E] and [W] are ester and water concentrations and the other quanti-
ties are as defined above. Therefore, [A][H] at equilibrium is $k[E][W]/k'$.
Values of [E], $k[W]$, and k' are in Tables I and IV of reference[4]. From
them the product [A][H] is calculated to be 8.2×10^{-7} mol^2/g^2 at equilib-
rium at 85°C and 25% RH. Consequently, [H] equals 8.2×10^{-2} if [A] equals
10^{-5} mol/g. A ten-fold greater acid concentration, which is twice the value
found for the binder of Tape 4, would require proportionately fewer alcohol
groups. Such concentrations seem impossibly large; pure butane diol, for
example, has a concentration of alcohol groups equal to about 2×10^{-2}
mol/g. Therefore, we think some process other than acid and alcohol react-
ing to give ester is required to explain the crosslinking observed by
Cuddihy at 0 and 15% RH[2] and by us at 0, 15, and 30% RH.

Our original speculation was that the iron oxide accounted for cross-
linking. However, data in the previous report showed that a sample of the
kind of iron oxide used in tape manufacture actually increased the hydroly-
sis rate of the polyester polyurethane.

Finding that extracted sol absorbs at 2250 cm^{-1} but that polyester
polyurethane does not, suggests that an additive which might cause the
crosslinking is present in the extract. Absorption between 2200 and 2300
cm^{-1} is not very common. Isocyanate and carbodiimide are two possibilities
and either could cause crosslinking if multifunctional. However, isocyan-
ates react with atmospheric moisture and the only polycarbodiimide we have
experience with absorbs at 2170 cm^{-1}. Therefore, such compounds seem to be
ruled out.

The cause of the crosslinking is still not known.

Apparently tape lifetime is limited more by binder adhesion than by
the sol content of the binder. Bertram and Cuddihy reported that tapes with
more than 1.5% sol, based on the total tape weight, became difficult to
use[3]. Tapes 3, 4, and 6 have more sol than that before aging and they
perform well. Furthermore, the sol content of Tape 4 does not change much
on hydrolysis. Thus sol content does not appear to be a useful quantity for
lifetime prediction. Binder adhesion has a large range, from more than 800
to about 2 N/m, with failure occurring somewhere between 10 and 50 N/m. The

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measured values are not very precise but the method probably can be improved. Some error in the prediction is tolerable because tape is marginally useful even after considerable loss of adhesion has occurred.

Our method of estimating tape lifetime will involve measuring binder adhesion after aging at different temperatures and humidities and correlating the measurements with the ability of the tape transport to process the tape. A decrease to some level of binder adhesion will be defined as ending tape life. Rates of decrease and tape lifetimes will be known as functions of temperature and humidity. Extrapolation by means of the Arrhenius relation will give values under the desired conditions. This approach is empirical but it is probably the best that can be done, given the variation in tape characteristics.

5.0 Future work

Aging of PET at 55 and 35°C will continue. The main effort will be to improve the infra-red method. Some work will be started to better understand the deterioration of the coatings.

Aging of model binder will continue at 60 and 35°C. The main concern will be whether variations with temperature and humidity extrapolate so as to change our conclusion that crosslinked polyester polyurethanes will eventually hydrolyze to useless materials at ambient conditions.

An attempt will be made to estimate the lifetime of magnetic tapes as outlined above. Experiments will be performed with extracts from tapes to try to understand the crosslinking mechanism.

6.0 Conclusions

PET films as currently made for photographic and electrographic use should last more than 1000 years if stored at 20-25°C and 50% RH. The lifetimes of the coatings, which bear the information, do not appear to be that long and are unknown.

Magnetic tape lifetime appears to be a function of binder adhesion. A program has been suggested to base lifetime prediction of magnetic tapes on variations of binder adhesion with temperature and humidity.

Experiments with crosslinked polyester polyurethanes indicates that these materials will not stabilize at a tolerable extent of hydrolysis even at low humidity. This conclusion is based on results at only one temperature, 85°C. Experiments are continuing at other temperatures with these materials.

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Table I

PET Films at 55 °C and 100% RH

Material	Time Days	T MPa	E %	$10^4[A]$ eq/g	k %/day
Film base	0	204	144	0.35	--
	586	190	128	0.44	0.037
	1105	165	106	0.54_i	0.039_i
Microfilm A	0	200	126	0.31	
	660_s	163	100		
	660	167	96		
	1105_s	166	90		
	1105	165	85		
Microfilm B	0	193	122	0.32	
	660_s	175	116		
	660	172	102		
	1105_s	171	88		
	1105	187	99		
Encapsulating Film	0	177	80	0.37	
	660	145	83		
	1105	151	73	0.57_i	0.039_i
Uncoated Electrographic C	0	116	185	0.41	
	660	110	142		
	1105	110	5	0.68_i	0.046_i
Coated Electrographic C	0	167	105	0.48	
	660	150	78		
	1105	140	68		
Coated Electrographic D	0	201	99	0.34	
	1040	177	70		

Subscripts:
i, From FTIR measurements; s, stripped of emulsion layer before aging.

Table II

Acid Content, Elongation at Break and Absorbance Difference[1]
in PET Aged in Boiling Water

Time Days	Elongation %	$[A]$ 10^4 eq/g	ΔAbs_1[2]	ΔAbs_2[3]
0	142	0.36	0.33	0.27
3	130	0.45	0.45	0.31
5.9	135	0.55	0.54	0.36
9.7	103	0.73	0.62	0.49
14.0	40	1.05	0.79	0.60
17.0	Brittle	1.41	0.98	0.76

Superscripts:
(1) From spectra of three stacked films, each 0.004 inch thick.
(2) ΔAbs_1 = Absorbance at 3542 cm^{-1} minus that at 3717 cm^{-1}.
(3) ΔAbs_2 = Absorbance at 3256 cm^{-1} minus that at 3717 cm^{-1}.

Table III

Initial Properties of Polyurethane Films

I/U mol/ratio	s fr	v fr	γ X ℓ/pol	T M Pa	E %	$\Delta Abs/\ell$ cm^{-1}
0	1	-	0	63	1200	6.8
0.14	0.79	0.054	0.6	73	900	5.8
.55	~0	0.38	42	45	370	0.045
1.1	~0	0.47	71	40	130	0.15

Table IV

Elemental Composition Change at 85 °C

I/U mol/ratio	Time Days	RH %	$10^5[A]$ mol/g	N %
0	0	–	1	3.6
0	48	100	80	5.6
1.1	0	–	<1	6.1
1.1	57	100	53	7.1
1.1	113	50	52	6.0

Table V

Recombination of Acid and Alcohol at 85 °C in Dry Polyurethane

(60 days except as indicated)

$$-(d[A]/dt) = k'[A]^2([H_o]+[A])$$

I/U mol ratio	$10^6 \ H_o$	$10^4 \ A_o$	$10^4 \ A$	$10^{-5} \ k'$ $g^2/mol,^2 d$ *
		----------mol/g----------		
0	100	5.1	1.9[†]	1.3
0	100	5.1	1.1[‡]	1.1
0	100	2.3	1.1	3.1
0.14	86	1.9	1.2	2.2, 2.1
0.55	0.67	2.5	1.75	1.4, 0.9
1.1	2.2	6.6	1.1	6.6, 4.2
1.1	2.2	1.25	0.59	18, 8.2
1.1	2.2	0.62	0.29	73, 22[3]

†) 68 d, ‡) 219 d, *) 2nd value uses $H_o = 10^{-4}$ mol/g

Table VI

Characteristics of Unaged Magnetic Tape

Tape	Binder Layer (BL) wt%	Sol Contact wt%	Binder Adhesion N/m[1]	Organic in BL wt%	Sol in Org BL wt%
1	20[2]	0.7	325	30[3]	8[4]
2	23	1.3	>800	24	24
3	32	2.4	150	25	30
4	24	4.6	>800	29	66
5A	28	0.7	>450	26	9.6
5B		1.0	35		
6		2.6	160		

[1] 1 N/m = 1.02 g/cm
[2] Not including the back coat that is 6% of the tape weight.
[3] Oxide binder only
[4] Assuming half the back coat is carbon.
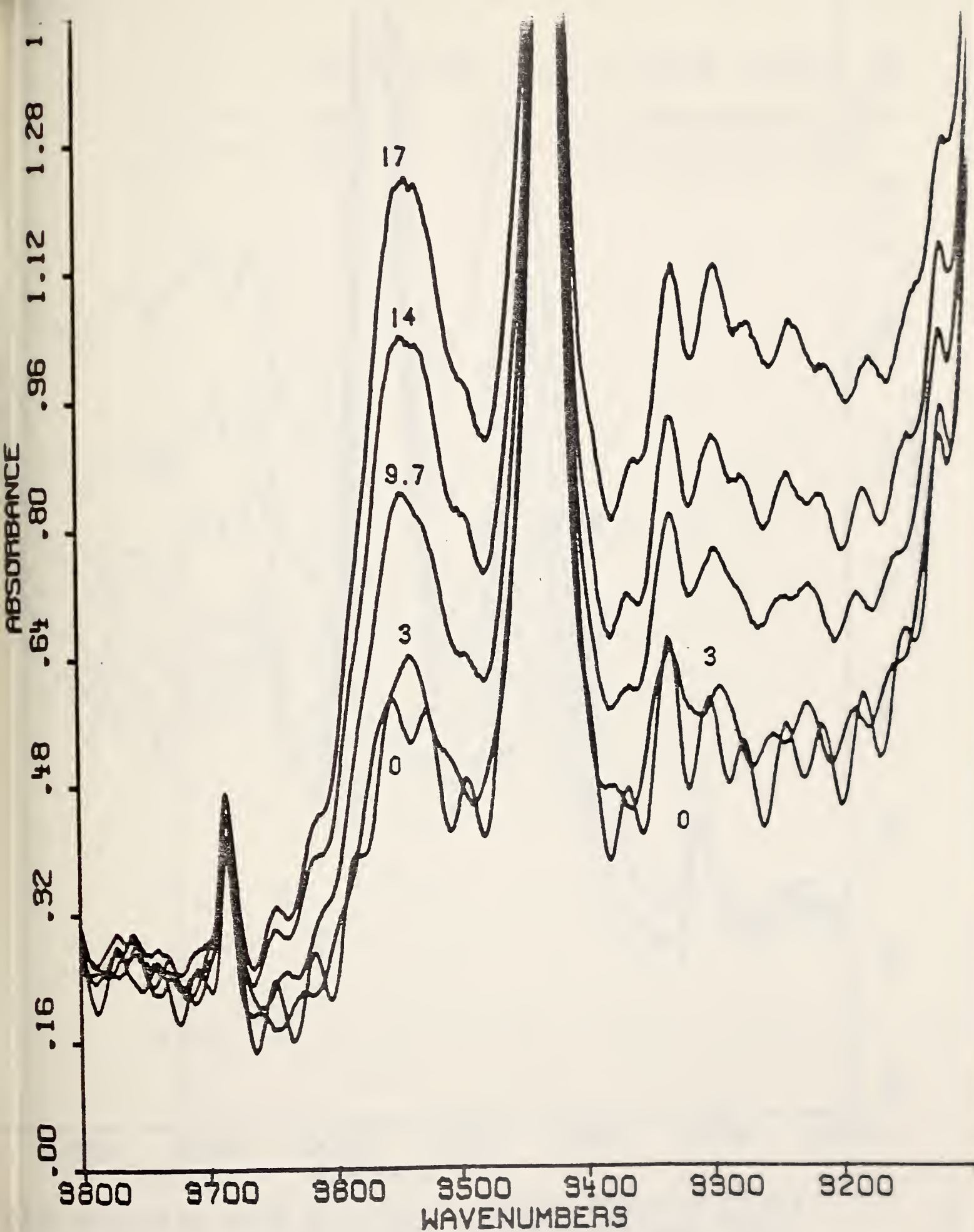
FIG. 1. INFRA-RED SPECTRA OF PET AFTER AGING IN BOILING WATER. 2-CM⁻¹ RESOLUTION. CURVES LABELED WITH AGING TIME IN DAYS.
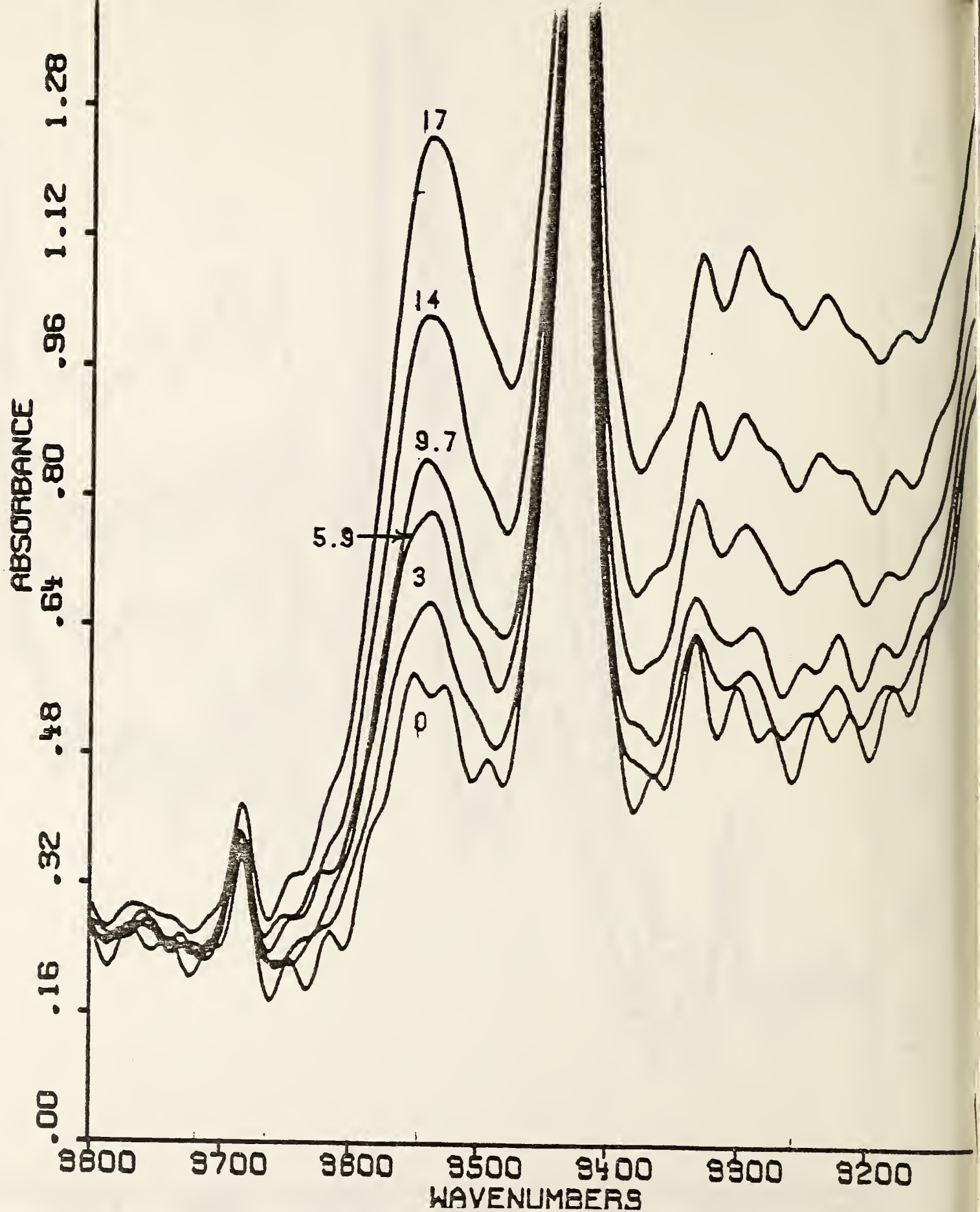
FIG. 2 INFRA-RED SPECTRA OF PET AFTER AGING IN BOILING WATER, 8-CM⁻¹ RESOLUTION. CURVES LABELED WITH AGING TIME IN DAYS,

FIG. 3 CHANGE IN [A] VS CHANGE IN ΔABS

□, —— AT 3542 CM⁻¹. LINE: [A]=1.69(Δ(ΔABS))−0.09
◇, — — AT 3256 CM⁻¹. LINE: [A]=2.11(Δ(ΔABS))−0.01
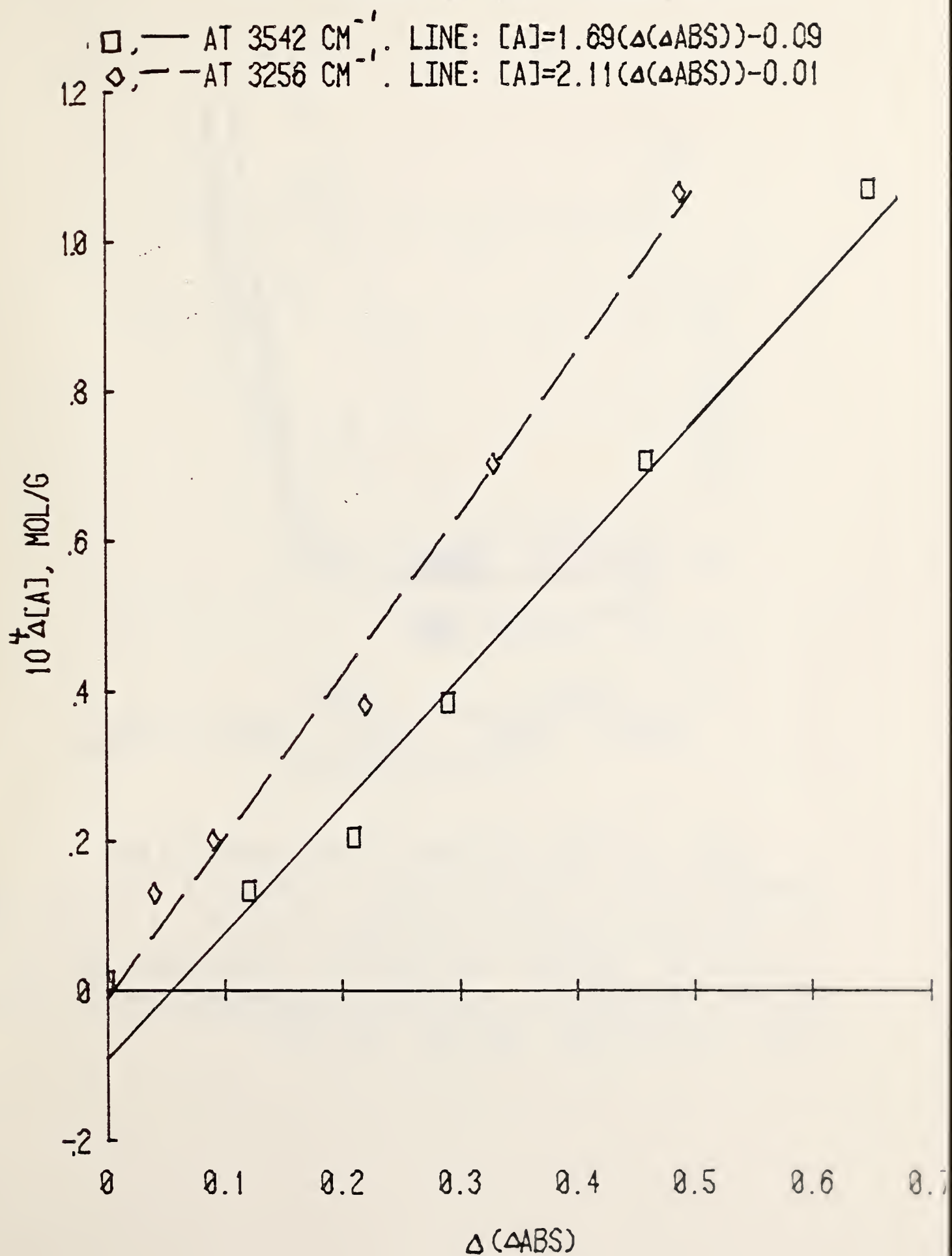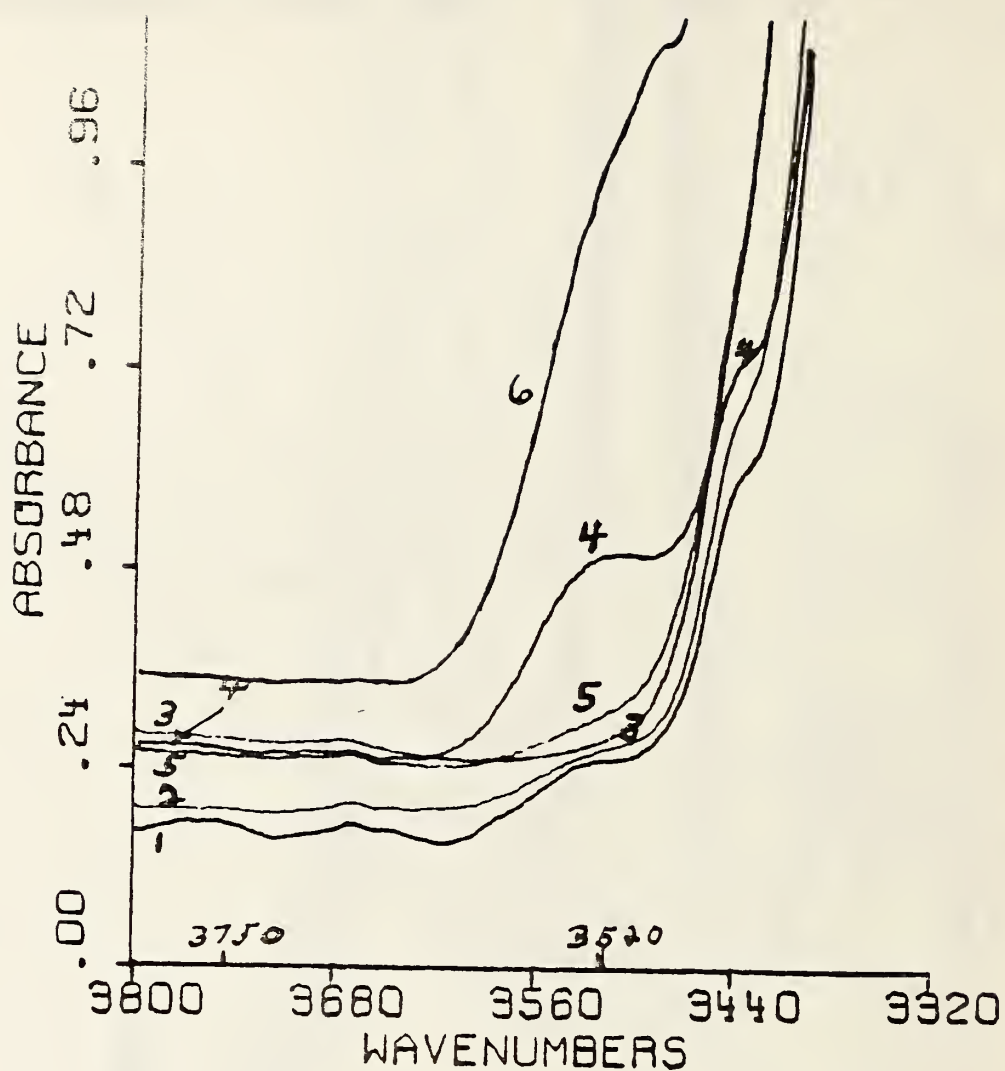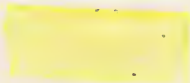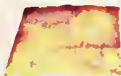
FIG. 4 FTIR SPECTRA OF URETHANE FILMS.
UNAGED: 1. I/U=0, l=0.012 CM; 2. I/U=0.14, l=0.013 CM;
3. I/U=0.55, l=0.015 CM. AGED AT 85°C: 4. I/U=0.14,
l=0.010 CM, 25% RH, 50 DAYS; 5. I/U=0.55, l=0.015 CM,
25% RH, 59 DAYS; 6. MULTIPLY ABSORBANCE BY 2, I/U=
0.55, l=0.015 CM, 50% RH, 87 DAYS.

FIG. 5

Color Development in Crosslinked Polyurethane,
(I/U) = 1.1, at 85 °C

	Unaged			
Dry N2	Dry Air	Wet Air	H_2O Vapor	Days
				18.7
				38.7
				56.7
		(25% RH)		239

FIG. 6 T AND E RELATIVE TO INITIAL VALUES
VS. DAYS AT 85 C AND 100% RH
T, UNSHADED SYMBOLS AND ——————— ;
E, SHADED SYMBOLS AND —— —— —— ;
△ , ▲I/U=0; + , ✳I/U=0.14; ▢, ▩ I/U=
0.55; ◇, ◆I/U=1.1.
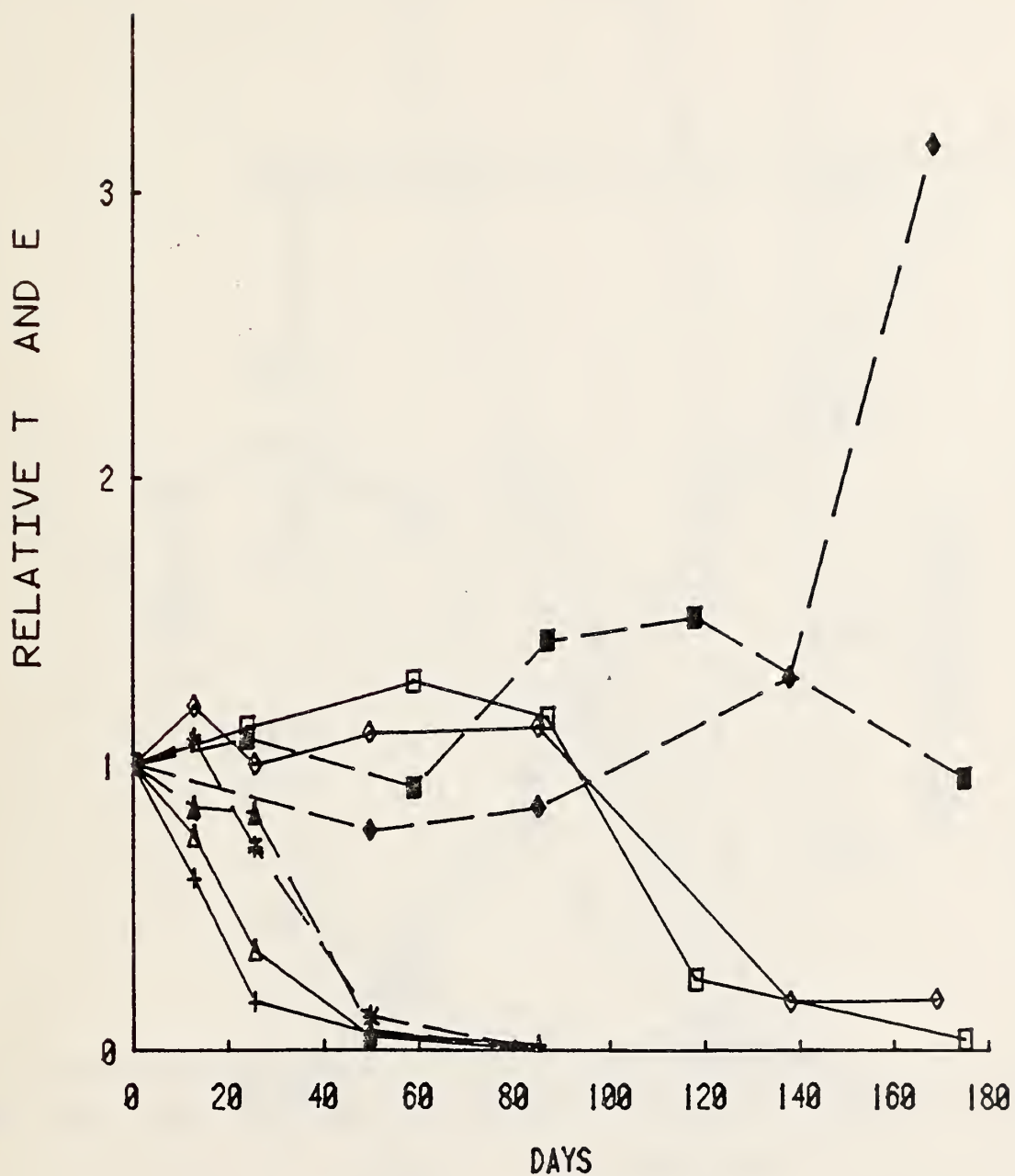
FIG. 7

T AND E RELATIVE TO INITIAL VALUES
VS. DAYS AT 85 C AND 25% RH
    T , UNSHADED,——; E, SHADED ,—— —;
  △ ,▲ , I/U=0; ✚ , ✳ , I/U=0.14;
  ☐ , ▓ , I/U=0.55; ◇ , ◆ , I/U=1.1
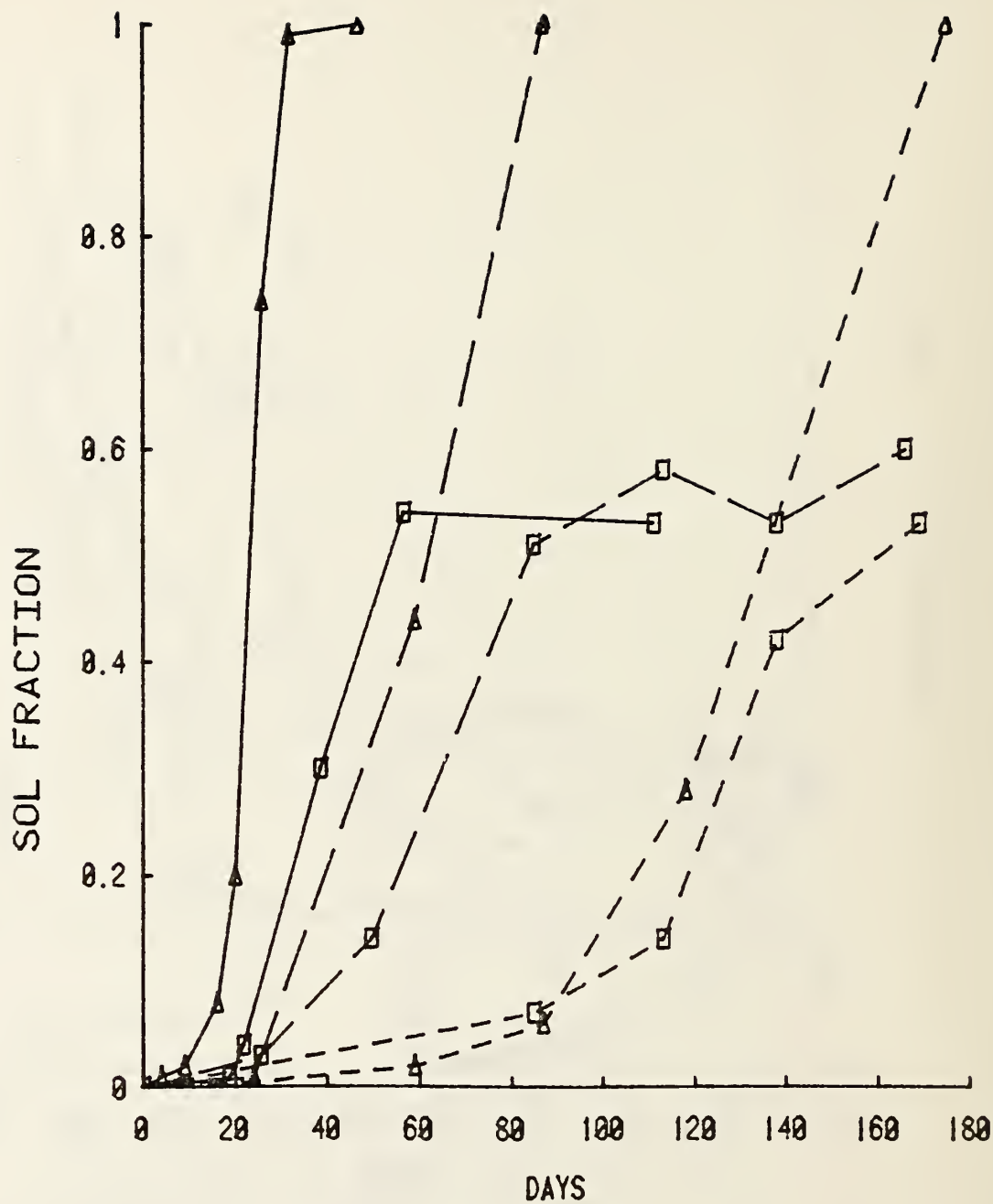
FIG. 8   SOL FRACTION VS TIME AT 85 C
△, I/U=0.55; □, I/U=1.1
100% RH ——— , 50% RH — — , 25% RH - - - -.
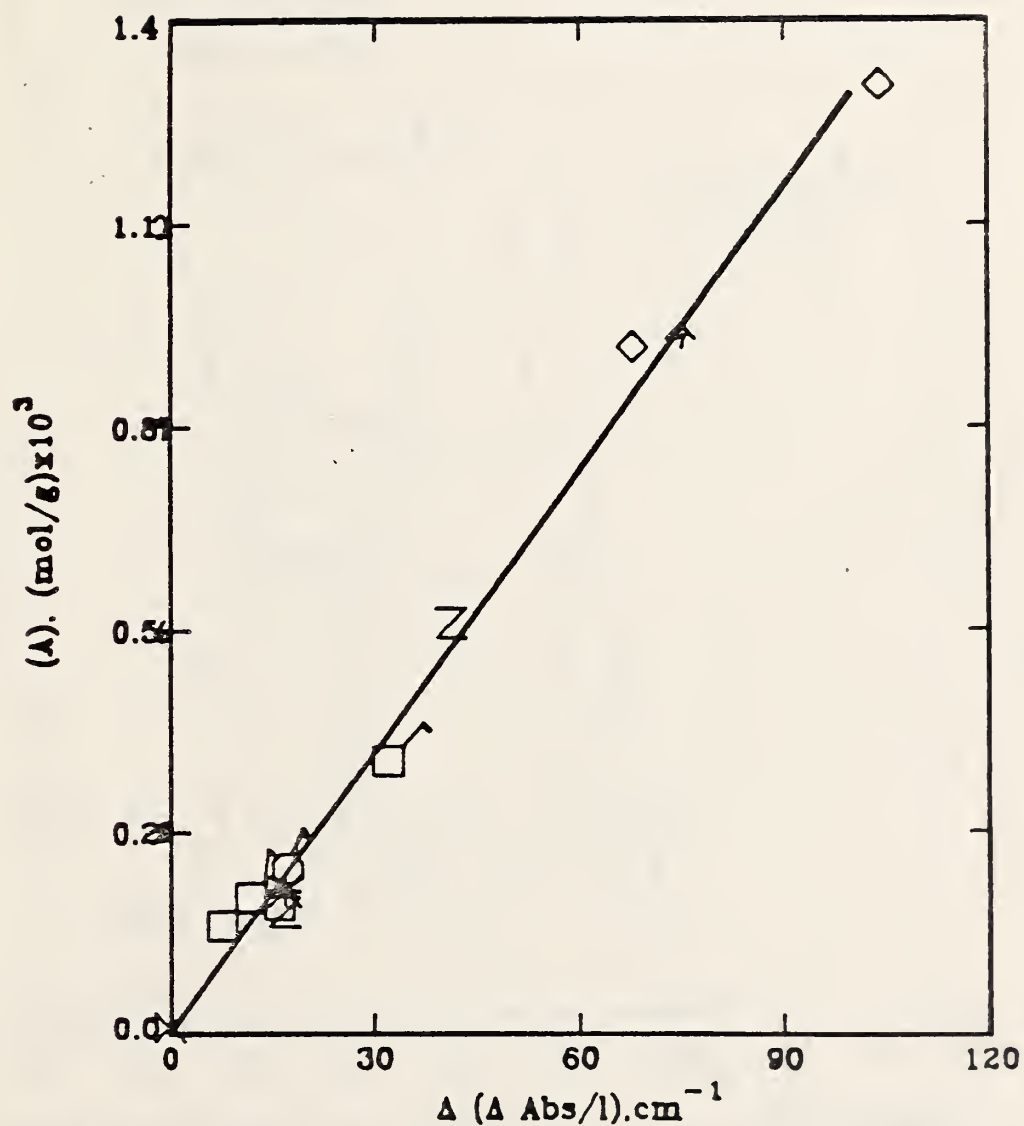
Fig. 9 Acid content vs. increase in Δ(absorbance/film thickness) during aging.

I/U=0:X,unaged; *,85C, 25% RH; ◌, 60C, 100%RH. I/U=0.14: ⊐,▦,Z; 85C, 100, 50, 25% RH;⊓, 60C, 100%RH. I/U=0.55: ◇,⬦; 85C, 100, 50% RH. Line: [A]=0.013X Δ(ΔAbs/l).
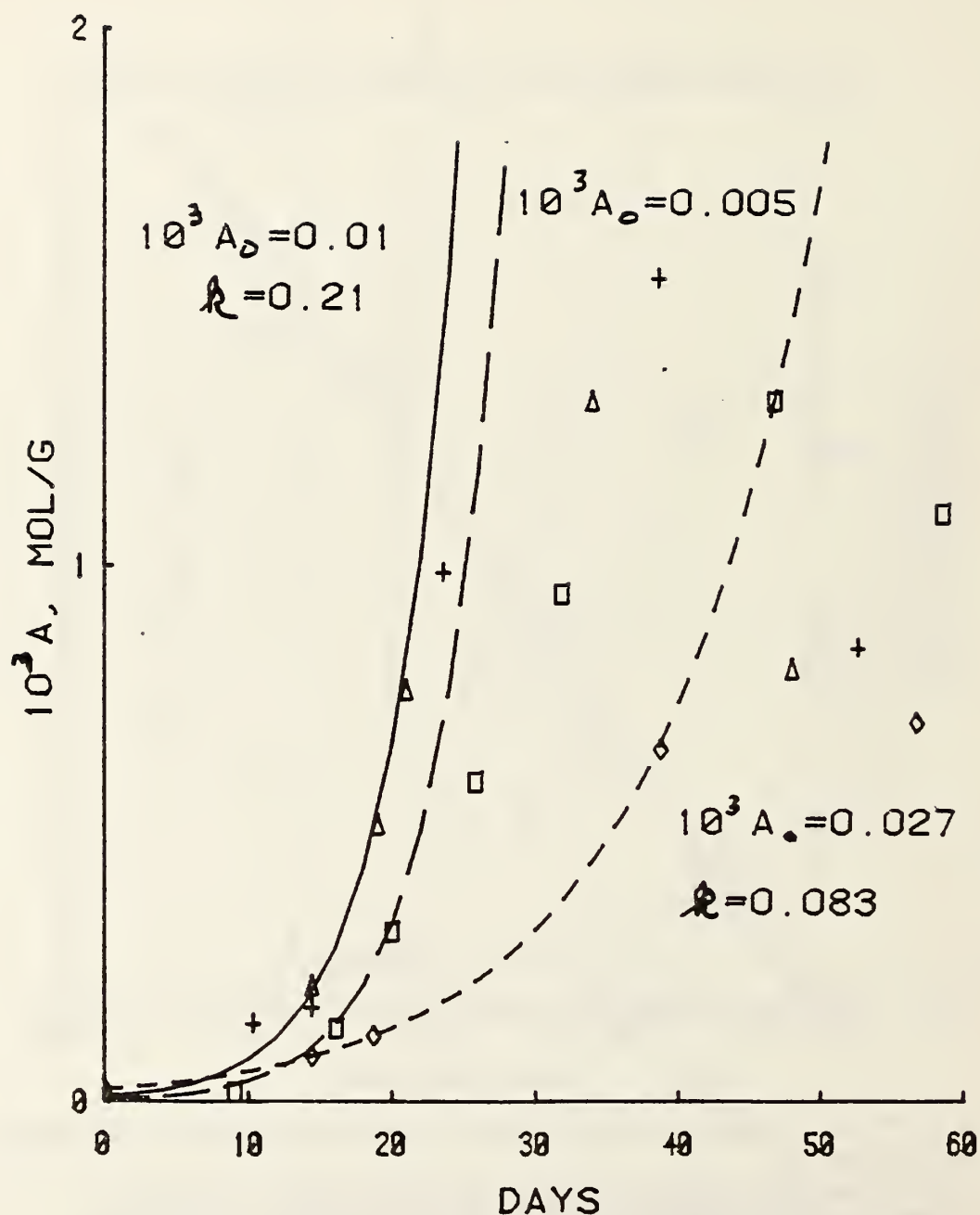
FIG. 10 ACID CONTENT VS DAYS AT
85 C AND 100 % RH
△, I/U=0; +, I/U=0.14;
□, I/U=0.55; ◇, I/U=1.1
LINES, A=A₀EXP(kt)
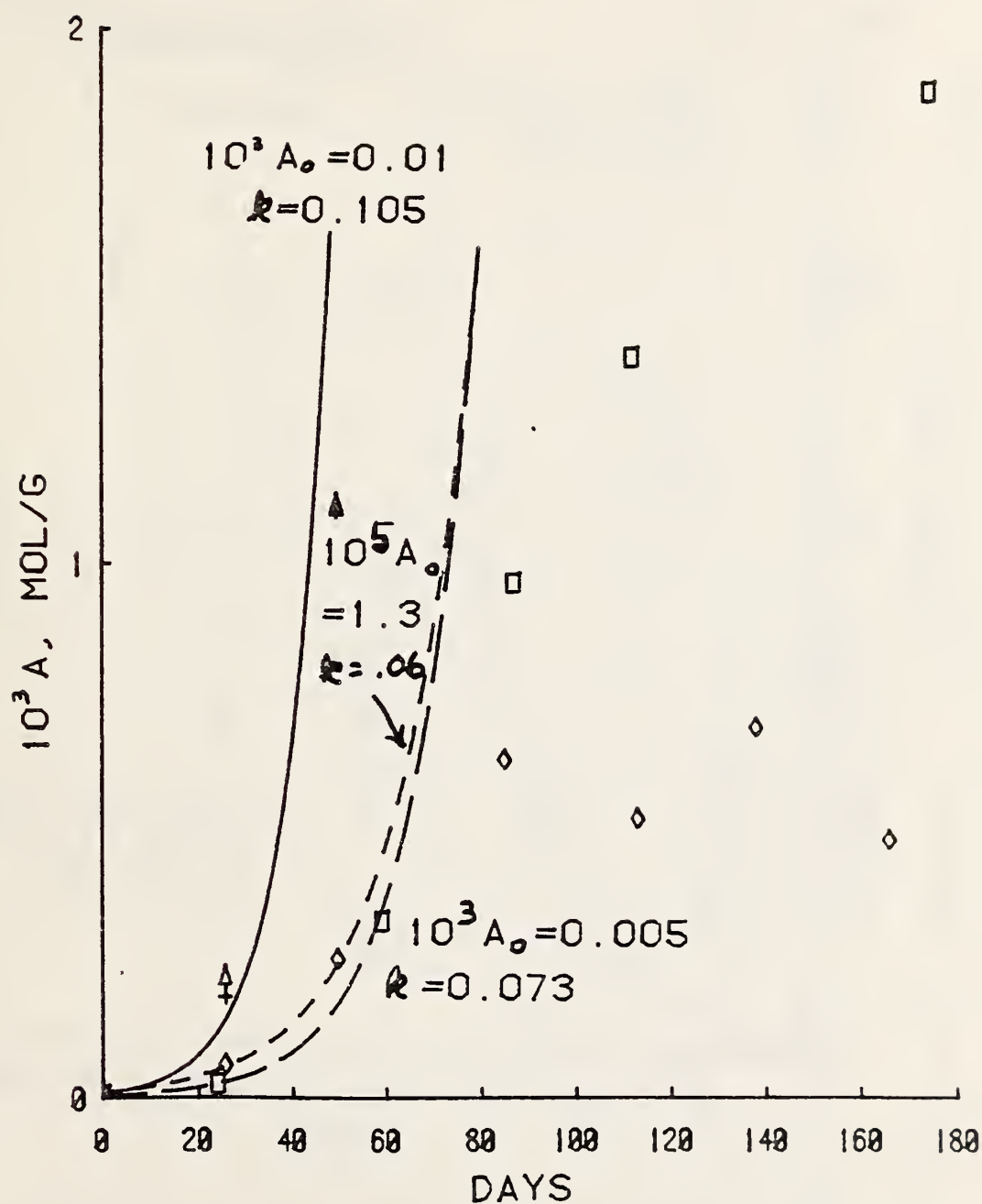
FIG. 11 ACID CONTENT VS DAYS AT
85 C AND 50% RH
△, I/U=0; +, I/U=0.14;
□, I/U=0.55; ◊, I/U=1.1
LINES, A=A₀ EXP(&t)
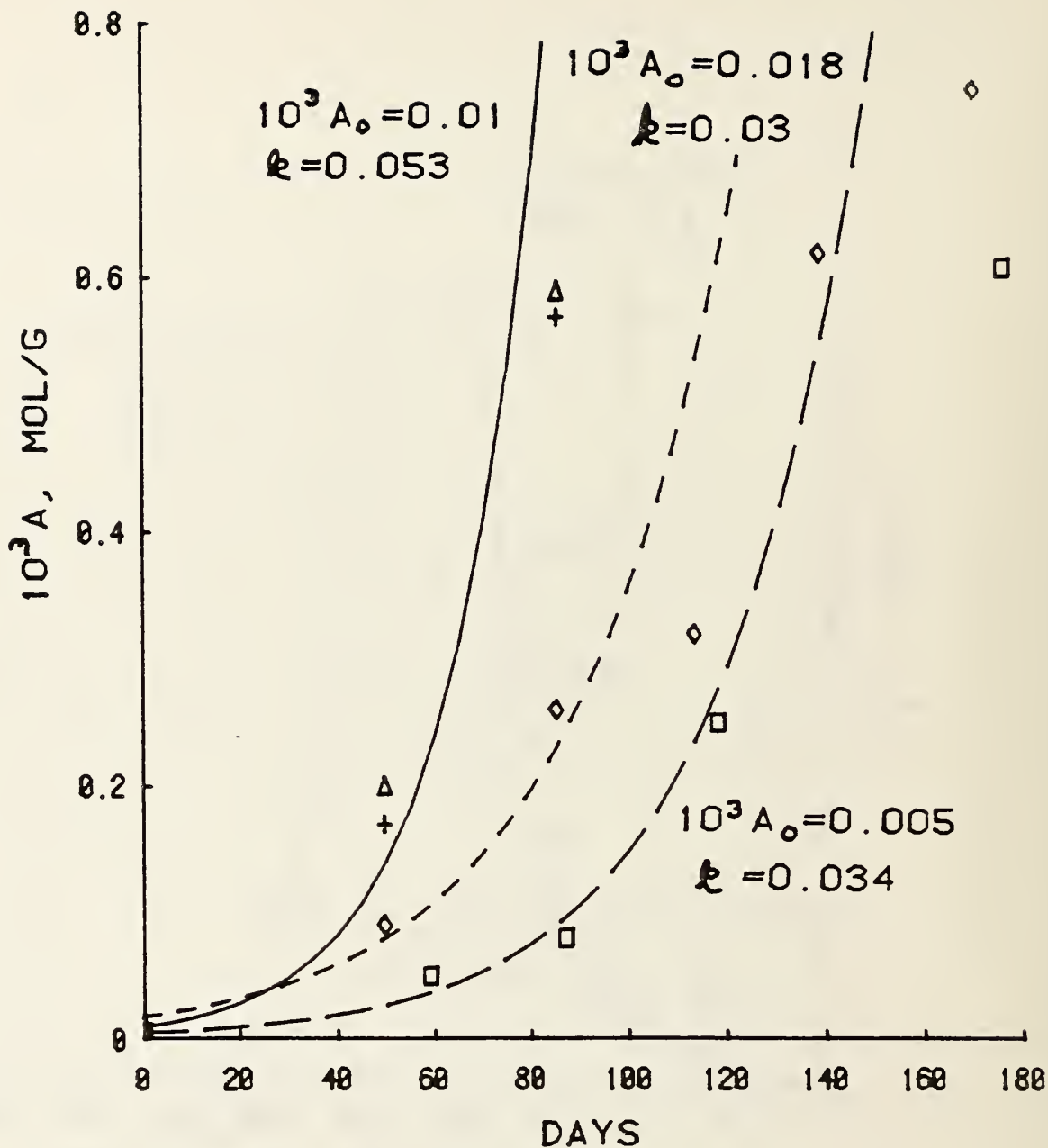
FIG. 12 ACID CONTENT VS DAYS AT
85 C AND 25% RH
△ I/U=0; +, I/U=0.14;
□, I/U=0.55; ◇, I/U=1.1
LINES, $A = A_o EXP(kt)$
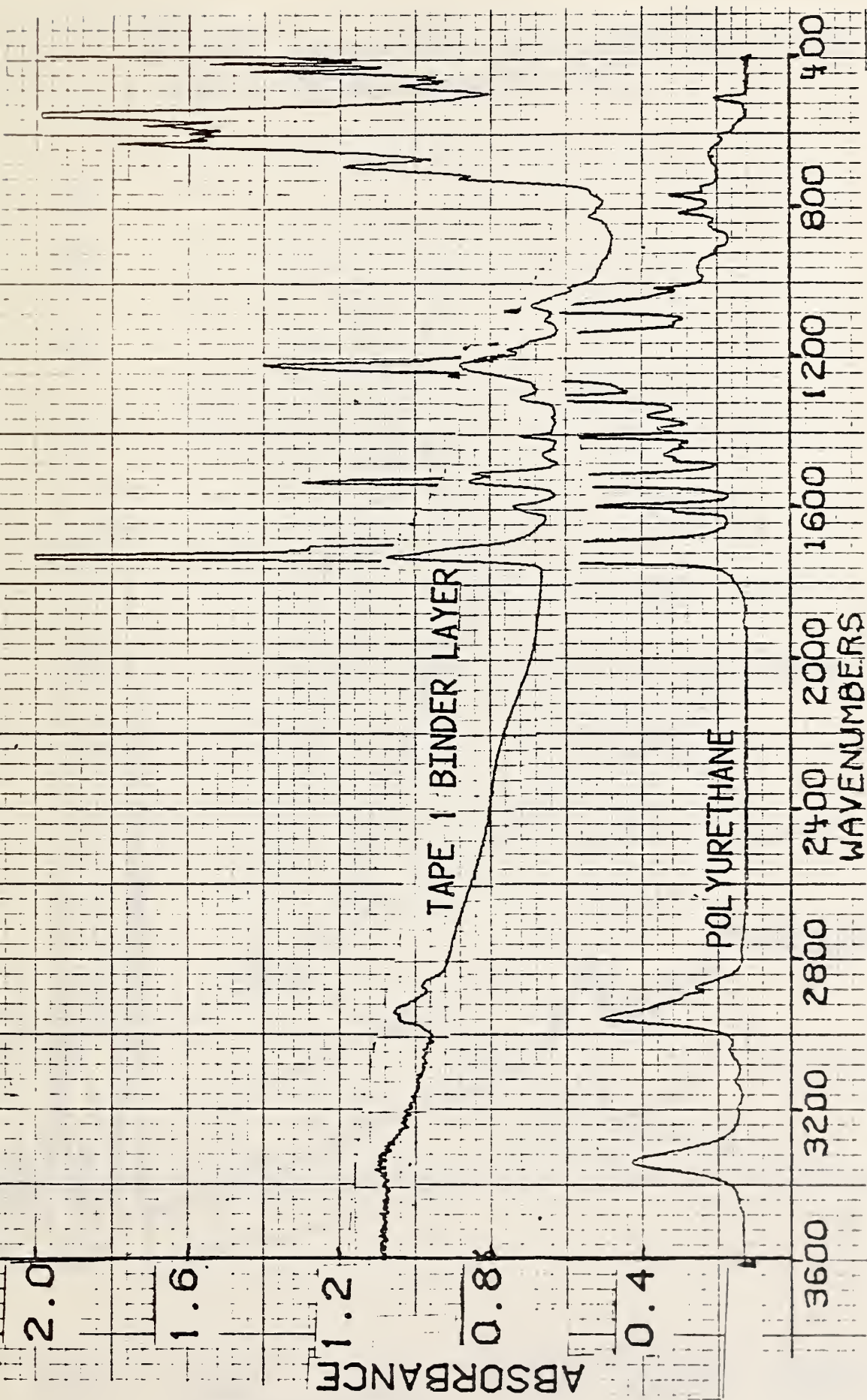
FIG 13 INFRA-RED SPECTRA OF BINDER LAYER AND POLYURETHANE

FIG. 14 INFRA-RED SPECTRA OF BINDER LAYER FROM MAGNETIC TAPES
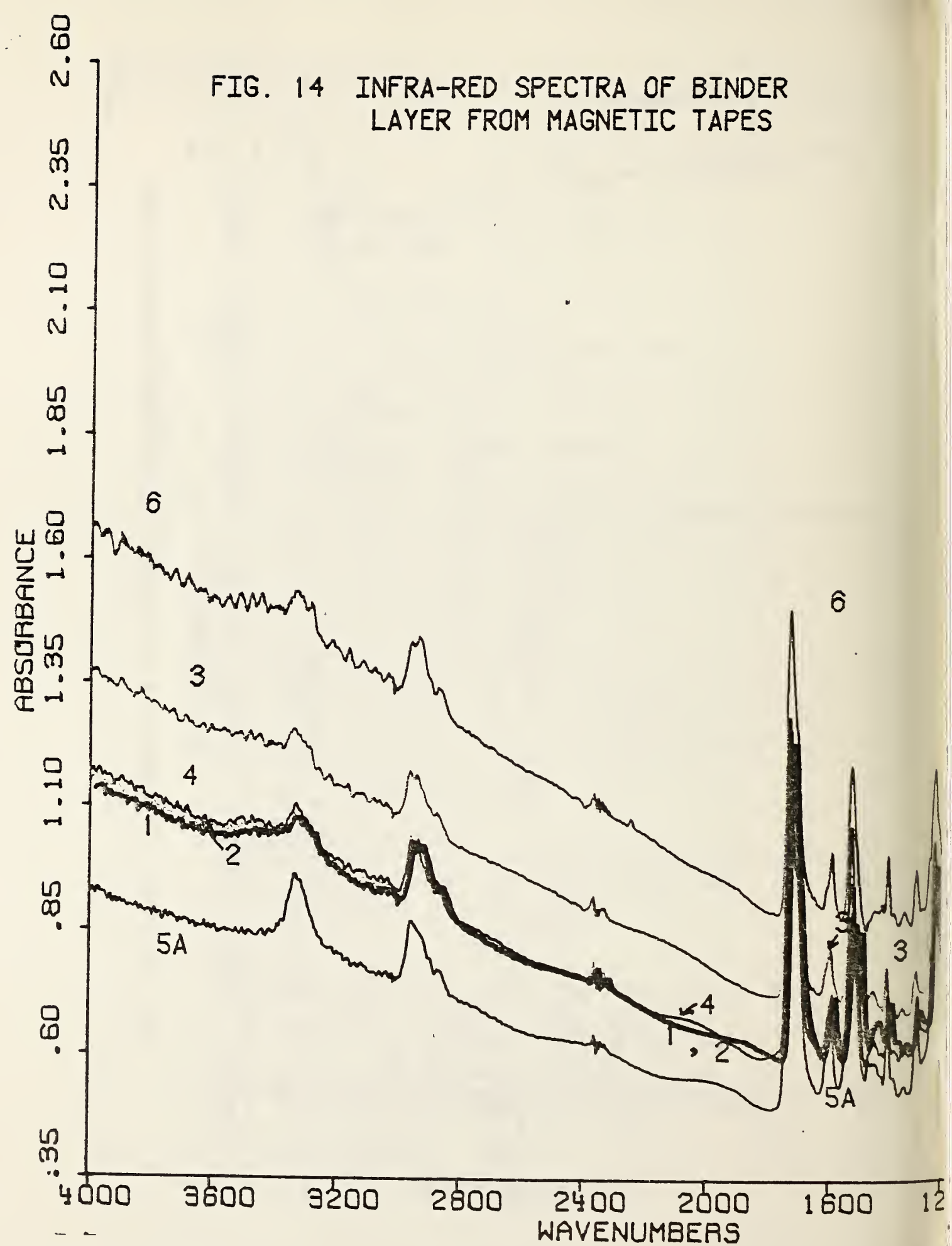
FIG 15 TAPE EXTRACT AFTER AGING AT 60 C AND 100% RH
1, △, ———— ; 2, □, ———— ; 3, ◇, ————
4, ▲, ——•—— ; 5A, ■, ——■—— ; 6, ◆, ——•——
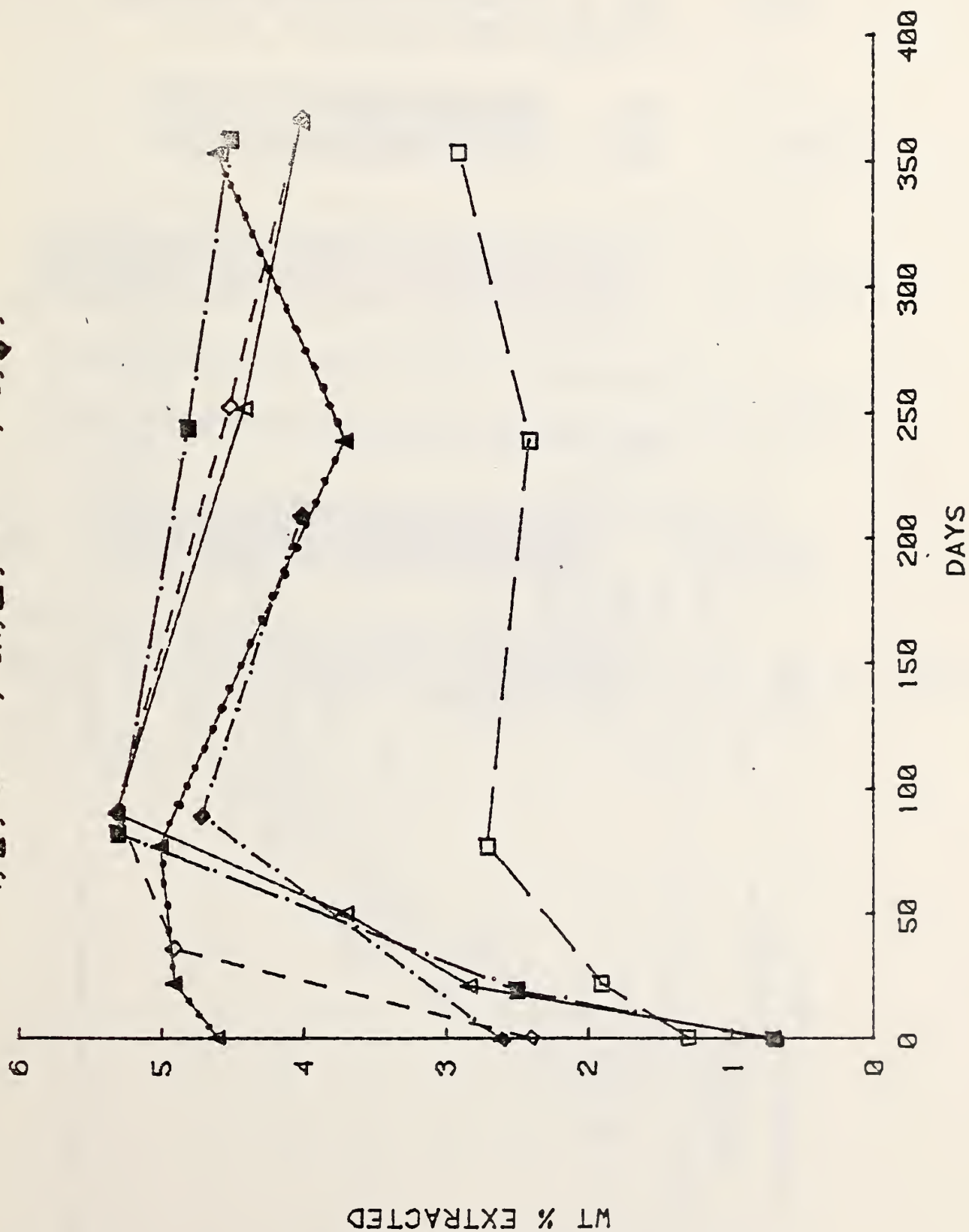
FIG. 16 RECORDER PLOTS DURING STRIPPING
OF BINDER LAYER FROM TAPES 1, 5A, 5B

TAPE 1, FULL SCALE 500G;
TAPE 5A, 1KG FS; TAPE 5B, 200G FS
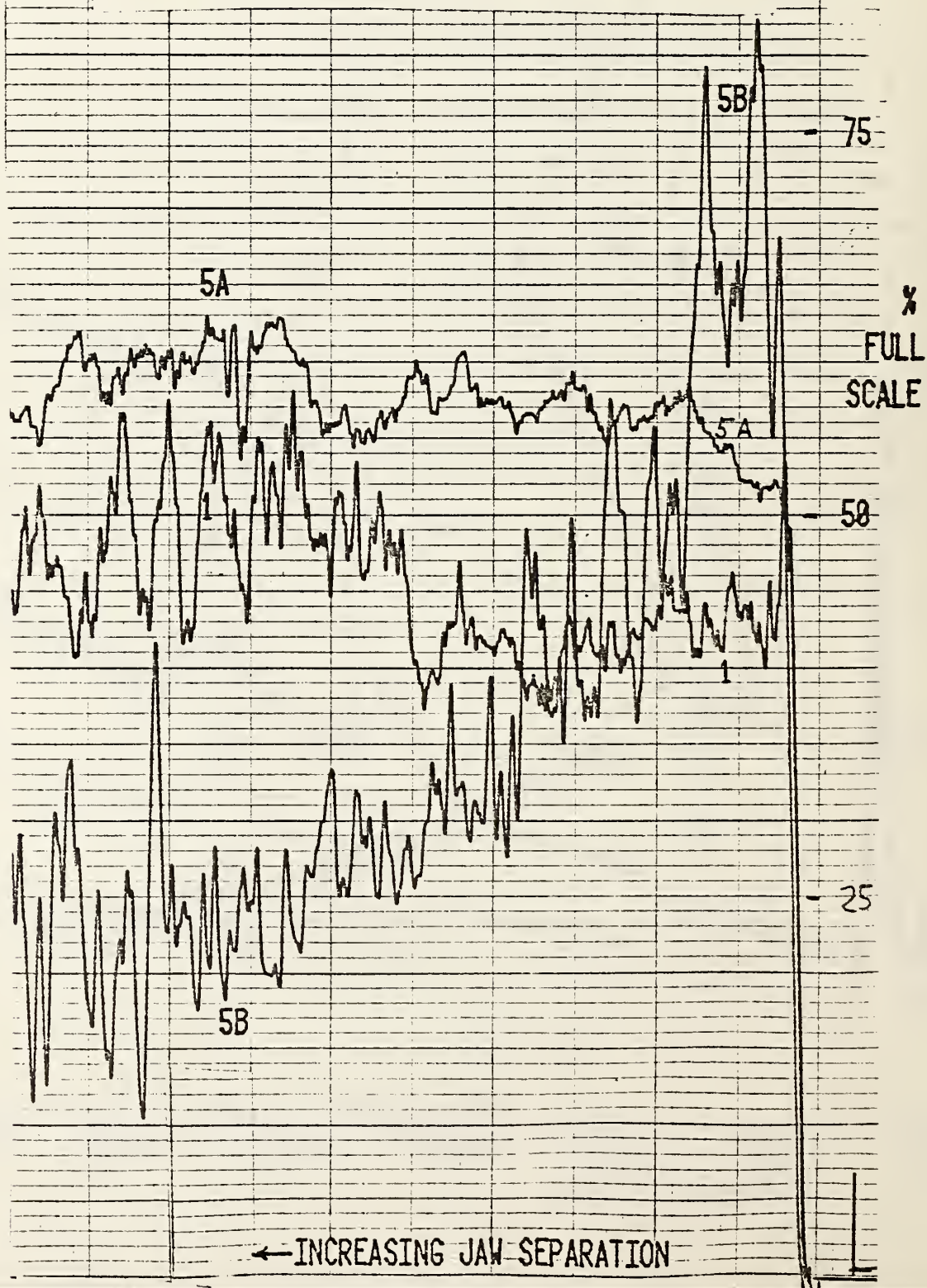
FIG. 17
STRIPPING PATTERNS OF BINDER LAYER

TAPE

1, UNAGED

3, UNAGED

5B, UNAGED

6, UNAGED

4, 60 C, 30% RH, 525 DAYS

N/M   100   290   250

FIG 18 BINDER ADHESION AFTER AGING AT 60 C AND 30% RH
1, △ ——————; 2, □ ————; 3, ◊ — — — ;
4, ▲ ············; 5A, ■ — · —; 6, ◆ — ·· —
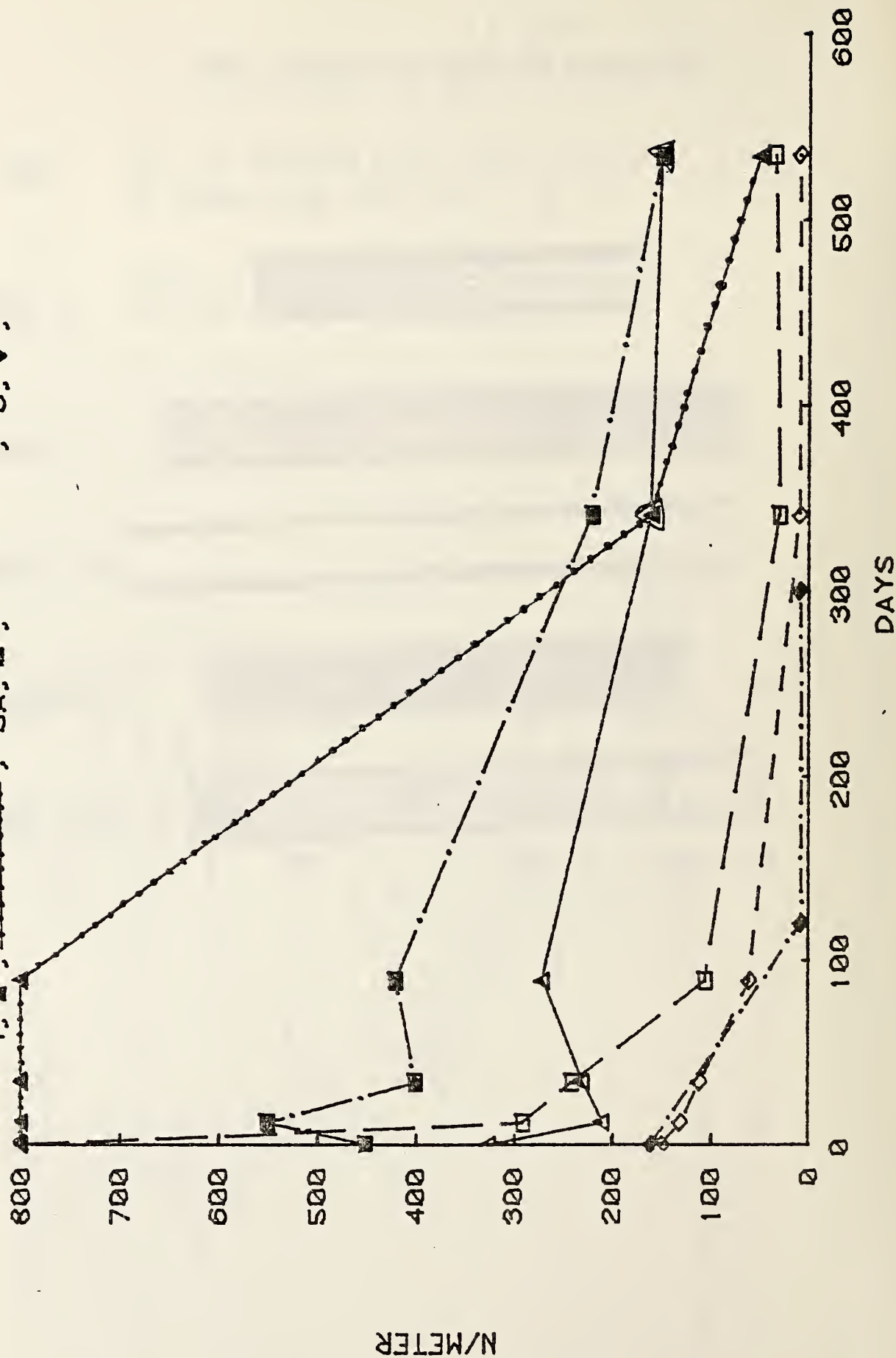
FIG 19 BINDER ADHESION AFTER AGING AT 60 C AND 15% RH
1, △ _____; 2, □ _____; 3, ◇ _____;
4, ▲ •••••••••; 5A, ■ _•_•_; 6, ◆ _••_••_

4. TITLE AND SUBTITLE

Prediction of the Long Term Stability of Polyester-Based Recording Media

5. AUTHOR(S)

D. W. Brown, R. E. Lowry, L. E. Smith

11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

Aging studies with poly(ethylene terephthalate) film base indicate the life-time is equal to about 1000 years if the material is stored at 20-25°C and 50% relative humidity. Concentration changes of acid and alcohol groups that occur as a result of aging have been measured by infrared analysis. Rate constants calculated by this method agree reasonably well with those calculated from acid contents determined by titration.

Crosslinked polyester polyurethanes were prepared as models of the binder of magnetic tape. Aging studies with these materials indicate that they hydrolyze more slowly than ordinary polyester polyurethanes. Samples aged at 85°C at 100, 50, and 25% relative humidity eventually deteriorated greatly in a physical sense.

Magnetic tapes were aged and measurements made of the sol content of the binder and its adhesion to the polyester base. The latter quantity appears to be a more valuable indicator of tape condition than sol content. Values of binder adhesion of six brands of magnetic tape initially varied between 800 and 35 N/m (or g/cm). Binder adhesion in aged tapes was less the higher the temperature and humidity of aging. A tape transport had difficulty processing tape with values of binder adhesion as low as 10 N/m. There was no problem at 35 N/m. It is anticipated that the lifetime of magnetic tapes can be predicted by measurements of binder adhesion.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

Hydrolysis; magnetic tape; polyester; poly(ethylene terephthalate); polyurethane